



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C02F 1/76, 1/00, 1/50	A1	(11) International Publication Number: WO 00/34186 (43) International Publication Date: 15 June 2000 (15.06.00)
(21) International Application Number: PCT/US99/27861 (22) International Filing Date: 23 November 1999 (23.11.99) (30) Priority Data: 09/205,168 4 December 1998 (04.12.98) US (71) Applicant (for all designated States except US): STELLAR TECHNOLOGY COMPANY [US/US]; 131 Byassee Drive, St. Louis, MO 63042 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): RAKESTRAW, Lawrence, F. [US/US]; 1714 Ashford Oak Court, Glencoe, MO 63038 (US). (74) Agent: LENNA, Leo, G.; Bryan Cave LLP, 245 Park Avenue, New York, NY 10167 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: SOLID WATER TREATMENT COMPOSITION AND METHODS OF PREPARATION AND USE		
(57) Abstract <p>The present invention relates generally to novel water treatment compositions and methods of preparation and use. More particularly, the invention relates to solid water treatment compositions containing at least one halogen source and at least one amine compound. Methods of preparing solid water treatment compositions and methods for controlling biofouling, disinfecting, cleaning and water systems are also provided.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**SOLID WATER TREATMENT COMPOSITION
AND METHODS OF PREPARATION AND USE**

5 BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to water treatment compositions and methods of preparation and use. More particularly, the invention relates to solid water treatment compositions comprising a halogen source and an amine compound, methods of preparing solid
10 water treatment compositions and methods for controlling biofouling, disinfecting, cleaning and water systems.

2. Description of Related Art

A wide variety of water systems are used for hygienic, recreational, commercial and industrial purposes. Typical water systems include cooling towers, swimming pools, spas,
15 decorative fountains, dehumidifiers, waste water treatment systems, air conditioning and refrigeration systems, boiler treatment, desalination, food processing, ground and surface water, industrial effluent, industrial process water, oil field and petroleum processing, paper and pulp processing, septic and sewage treatment, laundry cleaning and sanitation systems, sink sanitizer systems in bars and restaurants, hard surface disinfectant systems in food service areas,
20 disinfectant/sanitizer systems in the brewing industry, disinfectant systems for fruit and vegetable wash, ponds, reservoirs, potable water and toilets. A common problem associated with most types of water systems is contamination of the water by inorganic and organic debris entering the system. Water systems also provide conditions ideal for the growth of many types

of microorganisms. Formation of microorganism deposits is known as biofouling and can occur on almost any surface exposed to an aqueous environment. Biofouling causes energy loss from the system due to increased transfer resistance on the system surfaces.

Prior art approaches to controlling biofouling, disinfecting and cleaning water systems
5 include the use of hypohalite such as hypochlorites and hypobromites in various forms and combinations. As used herein, hypohalite refers to any compound that yields hypohalous acid, (HOX) or hypohalite ion (OX^- species wherein X is halogen when dissolved in water). Generally, a hypohalite source is added to the water to react with and eliminate contaminants. A specific concentration of free available halogen must be established and maintained for effective
10 biofouling control, disinfecting and cleaning.

Hypohalite species disinfect and clean water by reacting with debris and microorganisms that interfere with sanitary conditions in the water. The hypohalite species eliminate the contaminants by chemical oxidation that produces innocuous reaction products. Because there are many types of contaminants that can react with the hypohalite species, many possible
15 reactions can occur and a multitude of by-reaction products are formed. The majority of contaminants, however, comprise various forms of naturally occurring nitrogen compounds. The nitrogen compounds are destroyed by the reaction of the compound with hypohalous acid. The reaction results in the formation of nitrogen, carbon dioxide, water, chlorides and water soluble organic substances. As a result, the water is cleaned and sanitized.

20 The concentration of the hypohalite species can be determined by several methods and is commonly expressed in terms of parts per million (ppm) of free available halogen, generally chlorine or bromine. The optimum free available halogen concentration varies in a water system depending on the type of system and other environmental factors that must be taken into

consideration. Cooling tower water generally requires free and combined available chlorine from about 1.0 to 10 ppm; swimming pools generally require free available chlorine from about 1.0 to 5.0 ppm; spas generally require free available chlorine from about 3.0 to 5.0 ppm; toilet water generally requires free and combined available chlorine from about 2 to 30 ppm; potable water
5 generally requires free and available chlorine from about 2.0 to 3.0 ppm; and cleaning and sanitizing solution generally requires chlorine from about 100 ppm. The amount of free available chlorine or bromine necessary for treating a particular system is well known in the art.

The most economical and widely used source of free available halogen is gaseous chlorine as evidenced by the fact that it is used to disinfect > 99 % of the public drinking water
10 supplies and > 95 % of the municipal public swimming pools. Gaseous chlorine is inexpensive and has excellent disinfecting properties. The free chlorine residuals in the water are easy to maintain and monitor throughout the water distribution systems. However, the free chlorine residuals are unstable in bodies of water that are exposed directly to sunlight. The decomposition of the chlorine residuals is due the UV rays. The half-life of the chlorine residuals range from 2-4
15 hours depending upon the temperature of the water and the intensity of the sunlight. To maintain the optimum free chlorine residual in the water system, gaseous chlorine must be continually fed into the water system to replace the free chlorine lost to UV degradation and reactions involved in the disinfecting of the water. In addition, gaseous chlorine is hazardous and requires a high level of technical expertise to control the gaseous feed system and prevent the release of
20 hazardous amounts to the environment. As a consequence, other halogen sources are preferred over gaseous chlorine in many of the water treatment applications, particularly, residential, small public and private club swimming pools and mid-size cooling water recirculation systems.

Various attempts have been made to develop hypohalite-generating products that overcome the problems associated with gaseous chlorine. One of the most successful product developments has been the compressed forms such as, tablets, pucks, sticks, and the like of trichloroisocyanuric acid (TCCA). TCCA is now widely used to disinfect residential, small
5 public and private club swimming pools. TCCA has significant advantages over other products because it generates cyanuric acid which reduces the degradation of the free chlorine residuals by UV. Also, the free available chlorine content of TCCA is typically 90.5 % which is considerably higher (> 25 %) than other products, except gaseous chlorine which is 100%. In addition, it is easily compressed into solid forms that permit its use in simple low-cost dissolving devices such
10 as erosion feeders, floating feeders and skimmers to chlorinate the water continuously. Moreover, TCCA is safer to use than gaseous chlorine.

Despite TCCA's advantages over other chlorine products, disadvantages remain in its use in some water treatment applications. For instance, TCCA dissolves relatively fast in water. As a result, the concentration of the hypochlorite species in the water systems tend to be high, making
15 the water acidic and corrosive. Additionally, chloramines, which have objectionable odors, are generated. The combination of these properties has prevented TCCA from becoming widely used as a sanitizer in automatic toilet cleaning, spas and indoor swimming pool applications. TCCA can also form nitrogen trichloride, a very hazardous compound that detonates readily when subjected to small mechanical, electrical or thermal shocks. This disadvantage prevents TCCA
20 from becoming widely used in many cooling water treatment applications.

Attempts have been made to develop hypobromite products as an alternative to TCCA and other hypochlorite products. The most successful ones have been bromochlorohydantoins such as 1-bromo, 3-chloro-5,5-dimethylhydantoin (BCDMH) and a composition comprising 60

weight percent 1-bromo-3-chloro-dimethyl hydantoin, 30 weight percent dichloro-dimethyl hydantoin and 10 weight percent 1,3-dichloro-5-ethyl, 5-methyl hydantoin (BCEMH). For example, the BCEMH may comprise 60 weight percent 1-bromo-3-chloro-dimethyl hydantoin, 27.4 weight percent dichloro-dimethyl hydantoin and 10.6 weight percent 1,3-dichloro-5-ethyl, 5-methyl hydantoin and 1 weigh percent sodium chloride. These products are now more widely used in indoor swimming pools, spas, automatic toilet bowl cleaning and mid-size cooling water treatment applications than chlorine products, because they overcome the objectionable chloramine odor associated with chlorine products and are more effective with current alkaline treatment practices for cooling water re-circulation systems. However, the products still are not widely used to disinfect outdoor swimming pools because the free bromine residuals (HOBr and OBr⁻) are degraded very rapidly by UV rays and no suitable means has been devised to slow the degradation process significantly. Moreover, the cost of disinfecting water systems with bromine is at least two times as much as disinfecting with TCCA. In addition, a BCEMH type product has limited application in indoor swimming pools because it dissolves faster than the dominant bromine product, BCDMH.

Thus, TCCA could compete more successfully in the automatic toilet cleaner and water cooling treatment applications if a way is devised to control the dissolving rate of TCCA, reduce the acidity of the TCCA solutions, overcome the chloramine odor and resolve the nitrogen trichloride problem satisfactorily. In addition, BCEMH could compete more successfully with BCDMH if a way is devised to reduce the dissolving rate to a level similar to, or acceptably higher or lower than, that of BCDMH.

Thus, most water treatment compositions are limited in, or precluded from, use in some water treatment applications because of the inherent problems associated with the dissolving rate

of the compositions. The halogen source is often the most expensive material used in the composition making the compositions relatively expensive to manufacture. Other attempts to control the optimum free available halogen have concentrated on preserving the hypohalite species after it has already been released into the solution. Thus, none of the prior art attempts
5 have found satisfactory water treatment compositions with dissolving rates appropriate for a particular water system that are both convenient and cost effective to manufacture.

Thus, there is still a need in the art for a composition that can deliver a convenient cost effective water treatment composition with a controlled dissolving rate that is less corrosive to the water system without the undesirable halamine odor associated with compositions of the
10 prior art. Preferably, the composition should be readily customized for a particular type of water system.

SUMMARY OF THE INVENTION

The solid water treatment composition of the invention comprises at least one halogen source and at least one amine compound. In one embodiment, the solid water treatment
15 composition comprises a chlorine or bromine source or a combination thereof and at least one amine compound or combination thereof in a solid form wherein the at least one amine compound reduces the dissolving rate of the halogen source when water treatment composition is immersed in water or other aqueous solution, while maintaining the structural integrity of the solid form. The water treatment composition may further comprise a tableting additive.

20 Another aspect of the invention is a method of preparing the water treatment composition. The method provides water treatment compositions wherein at least one halogen source and at least one amine compound react when the solid water treatment composition contacted with water or other aqueous solution.

To further achieve the object of the invention, the invention provides methods of using solid water treatment compositions of the invention for disinfecting, cleaning and controlling biofouling in water systems.

Other features and advantages of the present invention will become apparent from the following description of the invention which refers to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows an apparatus used for the determination of steady state dissolving rates of candidate tablet compositions.

FIG. 2 shows the toilet apparatus used in the toilet flush system test.

FIG. 3 shows the decrease in weights for the composition of the invention comprising 10% by weight melamine and 90% by weight TCCA and BCEMH tablets during a toilet flush test.

FIG. 4 shows the decrease in weights for the composition of the invention comprising 20% by weight melamine and 80% by weight TCCA and BCEMH tablets during a toilet flush test.

FIG. 5 shows the decrease in weights for the composition of the invention comprising 30% by weight melamine and 70% by weight TCCA and BCEMH tablets during a toilet flush test.

DETAILED DESCRIPTION OF THE INVENTION

The solid water treatment composition of the present invention comprises a halogen source and at least one amine compound. The solid water treatment of the invention may also comprise tableting additives. Solid forms of the water treatment composition can be blended powders in packages, compressed granules, tablets, pucks, sticks, briquettes, pellets, extrusions, agglomerations, flakes, sheets, cast blocks, compressed blocks and the like.

As used herein, the "at least one halogen source" comprises one or more compound that provides hypohalous acid, HOX or hypohalite ion, OX⁻ species wherein X is halogen when

dissolved in water. The halogen source may comprise any halogen or a combination thereof. Halogen ion such as chlorine, bromine, and iodine may be particularly useful. Preferably, the halogen source comprises chlorine or bromine or a combination thereof. Representative halogen sources, for example, include trichloroisocyanuric acid (TCCA), dichloroisocyanuric acid (DCCA), monochloroisocyanuric acid, potassium dichloroisocyanuric acid, sodium dichloroisocyanuric acid dihydrate, anhydrous sodium dichloroisocyanuric acid, tribromoisocyanuric acid, dibromoisocyanuric acid, monobromoisocyanuric acid, monobromo-dichlorochloroisocyanuric acid, dibromo-monochloroisocyanuric acid, calcium hypochlorite, lithium hypochlorite, 1,3-dichloro-5,5-dimethylhydantoin(DCDMH), 1,3-dibromo 5, 5-dimethylhydantoin, 1-bromo, 3-chloro-5,5-dimethylhydantoin (BCDMH), 1,3-dichloro-5-methyl-5-ethylhydantoin, 1, 3-dichloro-5, 5-dimethyl-hydantoin, trichloromelamine, tribromomelamine. The at least one halogen source may further comprise a composition consisting of one mole of trichloroisocyanuric acid and four moles of potassium dichloroisocyanuric acid; compositions comprising sodium bromide and chlorine; compositions comprising a metal bromide and chlorine; compositions comprising trichloroisocyanuric acid and potassium bromide; and compositions comprising about 60% by weight 1-bromo-3-chloro-dimethyl hydantoin, about 30% by weight 1,3 dichloro 5,5 dimethyl hydantoin and about 10% by weight 1,3-dichloro-5-ethyl, 5-methyl hydantoin.

Halogen sources are readily available in commercial form. The most preferred halogen source is TCCA. However, it will be appreciated that the at least one halogen source is not critical, provided that the at least one halogen source yields hypohalite species capable of reacting with the at least one amine compound on or near the surface of the solid composition when the water treatment composition of the present invention is immersed in water.

As used herein, the amine compound can be any compound that has one or more primary amine groups (-NH₂) attached to a carbon atom that has amine functionality in the presence of hypohalite. The amine compound can be an aromatic amine, heterocyclic amine, condensed hydrocarbon amine, alkyl amine, organometallic amine and derivatives thereof or combinations thereof. The amine compound should be less soluble than the at least one halogen source. The amine group or groups of the compound must be reactive with hypohalite species produced when the water treatment composition of the present invention comes in contact with water. The amine compound can be substituted or unsubstituted provided that the amine nitrogen atom or atoms of the compound are available to react with hypohalite produced when the water treatment composition comes in contact with water. Preferred amine compounds comprise at least one amine group attached to a carbon atom of a ring structure. More preferred compounds are unhalogenated heterocyclic compounds comprising at least one amine group attached to a carbon atom of the ring structure wherein one or more atoms of the heterocyclic ring(s) is nitrogen, oxygen or sulfur. It is to be appreciated that while the preferred amine compound is unhalogenated, a halogenated compound may be used provided that the compound has amine functionality so that the amine nitrogen reacts with hypohalite species produced when the water treatment composition of the present invention is immersed in water. It is anticipated that combinations and mixtures of amine compounds may be used in the invention. Representative amine compounds are melamine and derivatives thereof, pyrimidine derivatives, piperazine and derivatives thereof, piperidine derivatives, piperidone derivatives, piperazine diones and derivatives thereof, pyridine derivatives, pyridazine and derivatives thereof, naphthyridines derivatives, anthracene derivatives, hydantoin derivatives, imidazole derivatives, imidazolidinone derivatives, glycoluril derivatives, oxazolidinone derivatives and combinations

or mixtures thereof. Preferred amine compounds comprise from one to three amino groups. The most preferred amine compound is melamine.

The present invention utilizes the amine nitrogen of the amine compound to react with hypohalite when the water treatment composition of the present invention is immersed in water or other aqueous solution. The at least one halogen source yields hypohalite species when the water treatment composition is immersed in water. The hypohalite species then reacts with the at least one amine compound forming halamine compounds on or near the surface of the solid water treatment composition. The resulting halamine reaction products have a dissolving rate slower than the at least one halogen source. The process continues as the halamine compounds dissolve and more at least one halogen source is exposed to the water yielding hypohalite species to react with the amine compound. The process continues until the solid water treatment composition is completely dissolved. Thus, the solid form of the invention maintains its structural integrity while providing an effective amount of halogen species in the water system.

The overall dissolving rate of the water treatment composition of the invention generally will be between the dissolving rate of the at least one halogen source and the amine compound. As a result of the slowed rate of hypohalous acid production, the hypohalous concentration in the water is less than would be obtained from solid forms comprising the at least one halogen source alone, such as TCCA. Further, halamine levels in the water are significantly reduced when the solid water treatment composition is used which in turn reduces objectionable halamine odors associated with using a halogen source alone. In addition, the reductions in the halamine concentration in the water decreases the potential to form hazardous amounts of nitrogen trichloride.

Solution pH levels when the water treatment composition is used generally will be higher than with using a halogen source alone. The amine groups behave like bases and react with hydrohalic acid (e.g. , HCl, HBr, etc.) reaction products to form amine halide salts thereby neutralizing the acids and making the solution pH of the water less acidic. The increased
5 solution pH level is less corrosive to components of the water system particularly valves and other mechanical parts which regularly come into contact with the water.

A particular aspect of the invention is the economical manufacture of the solid water treatment composition. Many amine compounds are less costly than typical halogen sources. Tableting additives can be added to the invention to aid in the economical manufacture and
10 effectiveness of the solid water treatment composition.

As used herein, tableting additives refer to agents such as bulking agents, dissolution control agents, pH control agents, flocculating agents, chelating agents, corrosion inhibiting agents, internal lubricating agents, hardening agents, non-oxidizing biocides, encapsulating agents, tableting aids, binders, perfumes, colorants, algacides, fungicides, and other ingredients
15 known in the art may be added to the water treatment composition of the present invention while maintaining the efficacy of the composition and without destroying the structural integrity of the solid form. The incorporation of additives can significantly decrease the manufacturing costs of the solid water treatment composition. For example, it has been discovered that certain metal salts such as metal sulfates, phosphates, carbonates, fluorides, and selected organic compounds
20 such as cellulose and derivatives thereof, polyethyleneoxide derivatives, polyoxypropylene-polyoxyethylene co-polymer derivatives, carbowax and derivatives thereof, having dissolving rates similar to or less than the halamine reaction products formed by the reaction of the at least one halogen source and the at least one amine compound can be incorporated into the water

treatment composition without destroying the structural integrity of the solid form. Calcium sulfate is particularly useful as an additive because significant amounts of expensive halogen source can be replaced with the metal salt while maintaining the efficacy of the solid water treatment composition of the present invention.

5 The water treatment composition of the invention can be formulated to be used in a wide variety of water system and aqueous media. The concentrations and ratios of the at least one halogen source and amine compound as well as the particle size and distribution will vary according to the system being treated. Any aqueous media or water system that can be treated with hypohalite can be treated with the water treatment composition of the present invention. An
10 advantage of the present invention is that the water treatment composition can be readily formulated to achieve the desired dissolving rate of the at least one halogen source. For example, BCEMH is widely used as an automatic toilet cleaning tablet because it has an acceptable dissolving rate and does not generate objectionable chloramine odors. The use of TCCA products in this application have been limited because TCCA dissolves faster than
15 BCEMH and generates objectionable chloramine odors. However, TCCA can be used in the compositions of the present invention to produce a product that has properties very similar to those of BCEMH by using TCCA in combination with an amine compound such as melamine. Furthermore, BCEMH has not been as widely used in the cooling tower market as BCDMH, because BCEMH dissolves faster than BCDMH. However, combinations of BCEMH and amine
20 compounds such as melamine in the solid water treatment composition of the present invention can produce a product that has properties similar to those of BCDMH. Further, the proper combination of TCCA and amine compounds such as melamine in the solid water treatment

composition of the present invention can be used to produce a product having properties similar to BCDMH.

The amount of at least one halogen source contained in the solid water treatment composition will depend on the amount of halogen necessary to treat a particular water system.

5 The halogen source may comprise as little as about 10%. The at least one halogen source generally comprises from about 20% to about 99% by weight of the solid water treatment composition depending on the halogen requirements of the system to be treated. Preferably, the at least one halogen source comprises from about 30% to about 95 % by weight of the solid water treatment composition. More preferably the at least one halogen source comprises about
10 20% to 85% by weight of the solid water treatment composition. For example, the most preferred amount of at least one halogen source is about 70% by weight of the solid water treatment composition when the composition is used to treat toilet water.

The amount of at least one amine compound contained in the solid water treatment composition is dependent on the amount of at least one halogen source and the desired dissolving
15 rate. The at least one amine compound must be in an amount effective to reduce the dissolving rate of the at least one halogen source by reacting with the hypohalite species to form halamine on or near the surface of the solid water treatment composition. The at least one amine compound may be in an amount as little as 1%. The at least one amine compound may comprise from about 1% to about 80% by weight of the solid water treatment composition. Preferably, the
20 amount of at least one amine compound can range from about 10% to about 60% by weight. Most preferably, the amount of at least one amine compound is about 20% by weight when the solid water treatment composition of the present invention is used to treat toilet water.

The amount of at least one tableting additives will vary depending on the amount of the at least one halogen source and the at least one amine compound used as well as the water system being treated. The amount of can be as much as, or more than 90% by weight of solid water treatment composition. Typical amounts of additives will range from about 5% to about 75% by weight of the solid water treatment composition. Preferably, the amount of additives will range from about 25% to about 75% by weight of solid water treatment composition. More preferably, additives will comprise about 20% by weight of solid water treatment composition. The most preferred tableting additive for toilets is calcium sulfate.

In a particularly preferred embodiment of the invention useful for cleaning toilet water, the at least one halogen source comprises about 70% by weight, the at least one amine compound comprises about 10% by weight and additives comprise about 20% by weight of the solid water treatment composition. The most preferred embodiment comprises about 70% by weight trichloroisocyanuric acid, about 10% by weight melamine and about 20% by weight calcium sulfate.

The water treatment compositions may be blended powders in packages or may be compressed, cast, agglomerated, extruded or molded into solid forms. As used herein, compacted tablets include, pellets, tablets, pucks, sticks, briquettes or other shapes formed by hydraulic or mechanical pressure sufficient to produce a solid form that maintains is shape. Compressed shapes can be unitary compacted tablets. The solid water treatment composition may also comprise a plurality of discreet granules. The discreet granules may contain at least one halogen source and at least one amine compound, The discreet granules may further comprise at least one tableting additive. Mixtures of discreet granules may comprise some granules containing at least one halogen source and at least one amine compound but no

tableting additive. The mixture of discrete granules may further comprise granules containing at least one tableting additive but no halogen source or amine compound.

The weight of the solid form will vary depending on the water treatment system being treated ranging from as little as 0.3 grams to over 800 grams. Generally, the solid water treatment composition tablets will weigh at least about 5 grams. It will be appreciated that different shapes and sizes can be manufactured for the different water treatment applications. For example, a solid form may be about 1/4" thick by about 1/2" in diameter or about 3" thick by 4" in diameter.

The solid water treatment compositions can be made from different particle sizes and by a variety of mixing, granulation and compressing methods. The preferred methods utilizes ingredient-blending techniques wherein the at least one halogen source and the at least one amine compound are combined to form an admixture. The admixture may further comprise at least one tableting additive. The admixture is compressed into a solid form by applying an effective amount of pressure. Typical pressures used to form compacted solid water treatment composition range from about 5000 to 20,000 p.s.i.

Preferably, similar size particles of the at least one halogen source and at least one amine compound are used. The at least one halogen source and at least one amine compound of the most preferred methods of producing the water treatment composition of the invention have particles less than 60 mesh U. S. standard screen. For example, when about 99% of the particles are finer than about 60 United States standard mesh screen, the admixture should be granulated into the preferred particle size before molding or forming into the solid water treatment composition of the invention. To form the preferred particle size, the admixture is compressed under sufficient pressure to form a flat solid composition or wafer. The flat solid composition is

then broken into particles of between about 10 and 60 mesh. The preferred particle distribution is about 99% greater than about 60 mesh and about 1% no greater than about 12 mesh. Pressure is applied to the admixture effective to form a solid water treatment composition.

Tabletting may be incorporated into the solid water treatment compositions. The preferred method of producing the solid water treatment composition comprising tabletting provides a first portion of the at least one halogen source and at least one amine compound and a second portion comprising tabletting additives. The first and second portions are compressed under an effective amount of pressure to form a first and second flat solid composition. The first and second flat solid compositions are broken into particles having particle distribution about 99% greater than second admixture is produced by admixing the additives separately from the n 60 mesh and about 1% no greater than 12 United States standard screen. The particles are then combined to form the admixture. The admixture may further be compressed under pressure sufficient to maintain a solid form typically from about 5000 to 20,000 p.s.i.

The solid water treatment compositions are used for disinfecting, cleaning and controlling biofouling of a water system. The present invention contemplates that the desired level of the at least one halogen concentration in a particular water system is readily ascertainable by one skilled in the art. The solid water treatment composition can be formulated to treat cooling towers, swimming pools, spas, decorative fountains, dehumidifiers, waste water treatment systems, laundry cleaning and sanitation systems, sink sanitizer systems in bars and restaurants, hard surface disinfectant systems in food service areas, disinfectant/sanitizer systems in the brewing industry, disinfectant systems for fruit and vegetable wash, ponds, reservoirs and toilets. The dissolving rate of the at least one halogen source can be easily controlled by adjusting the ratio of the at least one halogen source and at least one amine compound to slow the dissolving

rate of the at least one halogen source to the desired rate for the particular water system being treated.

For example, the optimum free available halogen concentration varies in a water system depending on the type of system and other environmental factors that must be taken into
5 consideration. Cooling tower water generally requires free and combined available chlorine from about 1.0 to 10 ppm; swimming pools generally require free available chlorine from about 1.0 to 5.0 ppm; spas generally require free available chlorine from about 3.0 to 5.0 ppm; toilet water generally requires free and combined available chlorine from about 2 to 30 ppm; potable water generally requires free and available chlorine from about 2.0 to 3.0 ppm; and cleaning and
10 sanitizing solution generally requires chlorine from about 100 ppm. The amount of free available chlorine or bromine necessary for treating a particular system is well known in the art.

The solid water treatment composition of the present invention can be readily formulated to provide the optimum free available halogen concentration. The solid water treatment composition may be introduced into the water of a water system by placing the composition in
15 direct contact with the water. The solid water treatment composition may also be placed in a holding device and then placing the holding device containing the solid water treatment composition into water.

EXAMPLES

The following examples further illustrate the present invention, and are provided as
20 exemplary but not restrictive as to the scope of the invention.

Example 1

Tablets were prepared by the following procedure. The desired portion of the granular ingredients are blended together and the compressed to form a compressed shape having the desired physical properties, e.g. 100 grams, 2.25" in diameter and 1" thick. For tablets having a composition of 79.21 weight percent TCCA, 19.80 weight percent melamine and .99 weight percent magnesium stearate, sufficient amounts of the respective ingredients are weighed separately to make tow tablets. Thus, 158.42 grams of TCCA, 39.60 grams of melamine and 1.98 grams of magnesium stearate are weighed separately and added to a glass jar. A lid was screwed on the jar and the ingredients were blended by hand tumbling the ingredients for five minutes. One tablet is made by taking a one hundred gram portion of the blended ingredients in a tablet punch die sets, and then placed in a laboratory hydraulic press where 30 tons of pressure is applied to the punches. The tablet is removed and stored in a sealed polyethylene container.

Example 2

The following procedure was used to customize the TCCA/melamine tablets. The procedure typically involved admixing the halogen source and the amine compounds, compacting the mixture and breaking up the resulting compact to form particles less than 1/4". An admixture of the other ingredients was processed in the same manner. The two admixtures were combined and blended by hand by tumbling the ingredients for five minutes. One tablet is made by taking a one hundred gram portion of the blended ingredients in a tablet punch die sets, and then placed in a laboratory hydraulic press where 30 tons of pressure is applied to the punches. The tablet is removed and stored in a sealed polyethylene container.

A tablet composition was made by combining 75.43 weight percent TCCA, 10.78 weight percent melamine, 12.93 weight percent calcium sulfate and .86 weight percent magnesium

stearate. Two 100 gram tablets were made by admixing 150.86 grams of TCCA with 21.56 grams of melamine by hand tumbling the admixture in a sealed jar for five minutes. The blend was then compressed to form thin wafers about 20 grams each that were then broken up with a mortar and pistil to form particles of $< \frac{1}{4}$ ". A second admixture was made by combining calcium sulfate and magnesium stearate and processed in the same manner. The two admixtures were combined and processed by the procedure in Example 1.

Example 3

The following experimental technique was used to assess the potential of candidate compositions. This was achieved by determining the steady state dissolving rates of tablets of given percent weights of the at least one halogen source and at least one amine compound in the equipment shown in Figure 1. In each test, a tablet was suspended in water flowing through the unit at a constant temperature (75°F) and a constant flow rate (75 ml/min). The total available halogen concentration of the water being discharged from the unit was determined every 30 minutes. Samples were taken from the discharge stream water at the sample port and the total chlorine measured with a DPD chlorine test kit. The total available chlorine concentration was recorded as parts per million (ppm) of total available chlorine. The total available chlorine measurements were continued until the first steady state condition was attained in the dissolving unit. The first steady state condition is defined as the point in time where the total available chlorine concentration stopped increasing and remained constant for two hours. At the first steady state condition, the tablet was dissolving in the flowing water at a rate fast enough to replace the available chlorine that was being removed from the unit by the discharge stream.

The following equation was used to determine the first dissolving rate of the tablets:

$$TDR_{ss} = \frac{TAC_{ss} \times A \times F_w \times B}{(AvC/100)}$$

where TDR_{ss} = The dissolving rate of the tablet at steady state, milligrams(mg)/min.
 TAC_{ss} = The total available chlorine of the water in the tablet-dissolving unit at
 steady state, ppm
 A = Conversion factor (ppm to milligrams per liter), mg/L/ppm
 F_w = Flow rate of the tap water to the tablet dissolving unit, cc/min (or
 mL/min)
 B = Conversion factor (millimeter to liter), L/ml

AvC = Available chlorine of tablet, %
 100 = Conversion factor (percent to weight fraction), %

The tablets used to generate the data by this technique weighed 100 grams each and measured approximately 1 inch thick by 2.25 inches diameter. All tablets were made by compacting blends of TCCA and melamine at 30 tons on a laboratory hydraulic press. Magnesium stearate (1 weight percent) was added to each tablet to aid in the compaction of the particles.

Example 4

The following example demonstrates the properties typically observed with TCCA tablets and tablets comprising varying weight percent amounts of TCCA and melamine. The total available chlorine concentration in ppm, the dissolving rate and solution pH levels were determined at the first steady state condition. The results are shown in Table I.

TABLE I

Steady State Dissolving Tests

On Tablets Comprising TCCA and Melamine

By % weight	Chlorine con. Ppm	Dissolving Rate mg/min	pH of unit water
TCCA 100	222	18.38	7.13
TCCA 90/M10	205	19.02	6.95
TCCA 85/M15	103	10.16	7.34
TCCA 80/M20	90.6	10.12	7.92
TCCA 70/M30	26.3	3.13	8.95
TCCA 60/M40	6.0	0.83	9.38

5 As can be seen from the data, after approximately 10 weight percent of melamine was added to the water treatment composition, the dissolving rate significantly decreased and the pH level increased. Thus, the dissolving rates and chlorine concentrations of TCCA can be controlled by the addition of varying percent weight amounts of melamine to the water treatment
10 composition.

Example 5

The following example shows the first steady state dissolving rate of tablets comprising various weight percent amounts of BCEMH and melamine having the same dimensions at the
15 TCCA tablets. The tables were tested under the same conditions as the TCCA/melamine tablets. The chlorine concentrations and dissolving rates were determined at the first steady state condition. The results are summarized in Table II.

TABLE II

Steady State Dissolving Tests

On Tablets Comprising BCEMH and Melamine

By % weight	Chlorine conc. ppm	Dissolving Rate mg/min
BCEMH 100	75	9.992
BCEMH 90/M 10	66.7	9.200
BCEMH 85/M 15	57.6	8.420
BCEMH 80/M 20	36.3	5.630
BCEMH 75/M 25	15.4	2.550
BCEMH 70/M 30	8.5	1.490

5 As can be seen by the test results, the steady state dissolving rates of tablets made from BCEMH and melamine decreased from about 9.99 to 1.49 mg/min as the melamine content of the water treatment composition increased from 0 to 30 wt %. These results demonstrate that the dissolving rate of BCEMH tablets can be customized to produce tablets with dissolving rates lower than tablets comprising BCEMH alone, by adding melamine in varying percent weights.

10

Example 6

A toilet flushing test was utilized to evaluate the average dissolving rate, the effect on the chemistry of the water and the chlorine content of the air over the water of the toilets treated with the water treatment composition tablets of the present invention and BCEMH tablets. Each test consisted of placing two tablets of the water treatment composition in one toilet and two tablets
 15 BCEMH in another toilet. Figure 2 is a schematic of the toilet design. As shown, both toilets were connected to a common source of tap water so that the temperature and the chemistry of the water were the same for each toilet. Each water line was equipped with a solenoid valve that could be opened and closed at a predetermined frequency and duration by a programmable actuator. The toilets were flushed every 30 seconds for 16 hours (2,000 flushes per 16 hours).

The flush cycles were then suspended for 8 hours. The tank of each toilet was equipped with two ports. One port was used to determine the chlorine content of the air in the headspace of each toilet could be determined during each suspended flush cycle. The other port was used to obtain samples of the water in each toilet tank near the end of each suspended flush cycle.

5 The chlorine content of the air of the head space of each tank was determined with Gastec Passive Dosimeter Tubes For Chlorine, which were inserted through a rubber stopper in each gas sampling port, at the fourth hour of the suspended flush cycle. The tubes were removed before the end of the seventh hour of the suspended flush cycle. The chlorine reading in ppm was divided by the number of hours the dosimeter tube was left in the gas sampling port.

10 Water samples were taken from each toilet tank after the chlorine gas sampling tubes were removed. The pH and the total available chlorine concentration were then determined. The pH was determined with a standard laboratory pH meter. The total available chlorine concentration was determined by the same method described above.

The tablets were removed at the 7th hour, carefully patted with absorbent paper towels to
15 remove excess moisture and weighed. The tablets were repositioned in the respective toilets just before the 16th hour flush cycle was re-initiated.

The average dissolving rate of each tablet was determined by the formula shown below:

$$\text{TDR}_{\text{TFT}} = (W_1 - W_2) / TC$$

where, TDR_{TFT} = average dissolving rate of tablet for time, T, grams/hour

20 W_1 = weight of tablet at start of toilet flushing test, grams

W_2 = weight of tablet at time, T, grams

T = time, days

C = conversion factor, 24 hours/day

Note, two tablets of each composition were typically used in a toilet flushing test. Thus, the average dissolving rate for two tablets can be calculated by adding the average dissolving rates of each tablet and dividing by two.

In the following examples, BCEMH tablets were used as the reference composition in each test. The dimensions, the shape and the weights of the BCEMH tablets and the water treatment compositions of the present invention were essentially the same in each test.

Example 7

Data were generated to compare the average dissolving rates for TCCA tablets with those of the bromine product referred to as BCEMH tablets under the conditions described above in EXAMPLE 4. The water temperature was 58-66°F during the test. The data showed that the TCCA tablets dissolved faster than the BCEMH tablets. For example, the weights of TCCA tablets decreased from 99.9 and 100.1 to 36.9 and 36.3 grams, respectively over a period of 11 days. The average dissolving rate of each TCCA tablet under these test conditions were calculated to be 0.239 and 0.242 gram/hour, respectively. The average dissolving rate of the two TCCA tablets was determined to be 0.241 gram/hour. The data also show that the weights of the BCEMH tablets decreased from 100 and 99.9 to 62.3 and 55.2 grams, respectively. The average dissolving rate of each tablet was determined to be 0.142 and 0.169 gram/hour. Thus, the average dissolving rate of the two tablets was 0.156 gram/hour.

The total available chlorine concentration in the toilet water treated with TCCA tablets was found to decrease from 75 to 29.2 ppm during the test. For the BCEMH tablets, the total available halogen concentration (as available chlorine) ranged from 8.3 to 16.7 ppm.

The chlorine concentration in the air inside the toilet tank above the water treated with the TCCA tablets was determined to be 2.9 ppm after one day. Although it decreased to zero by the

next day, a strong chloramine odor was present in the toilet flushing test room throughout the test. Also, the chloramine odor was overpowering when the TCCA tablets were removed each day for weighing. Chlorine was not detected by the Gastec Passive Dosimeter Tubes in head space of the toilet tank containing the BCEMH tablets.

5 The pH of the water treated with TCCA tablets ranged from 7.28 to 8.70, whereas it ranged from 8.69 to 9.60 in the water treated with the BCEMH tablets.

Example 8

Data were generated to obtain a comparison between the average dissolving rates for TCCA/melamine (90/ 10 % weight) water treatment composition tablets and reference BCEMH
10 tablets under the conditions described above. The water temperature during the run was 45-48°F. Figure 3 shows the decrease in weights of both types of tablets with time. The data show that the TCCA/melamine tablets dissolved faster than the BCEMH tablets. For example, the weights of the TCCA/melamine tablets decreased from 100.4 and 100.7 to 73.1 and 76.2 grams, respectively over a period of 8 days. The average dissolving rate of the tablets was calculated to be 0.17986
15 grams/hour. The data also showed that the weights of the BCEMH tablets decreased from 101.5 and 101.6 to 84.3 and 86.8 grams, respectively over the same period and conditions. The average dissolving rate of the two tablets was calculated to 0.1111 grams/hour.

The total available chlorine concentration in the TCCA/melamine water treatment composition toilet water was found to decrease from 33.3 to 29.2 ppm during the test. For
20 BCEMH tablets, the total available chlorine in the water fluctuated between 18.7 and 20.8 ppm.

The pH of waters in the toilet tanks, ranged between 8.59 and 9.27 for the TCCA/melamine tablets and between 8.30 and 9.32 for the BCEMH tablets.

Example 9

The following example shows that the dissolving rate of TCCA/melamine tablets could be made to dissolve slower than BCEMH tablets by increasing the melamine content of the TCCA/melamine compositions. The TCCA/melamine (80/20 % weight) water treatment composition tablets were compared to BCEMH tablets. The water temperature during the test was 42-46°F. The test data shown in Figure 4 show that the tablet weights of the TCCA/melamine tablets decreased from 100.5 and 100.4 to 88.2 and 86.1 grams, respectively during 8 days of the test. The average dissolving rate of the tablets was calculated to be 0.0696 gram/hr.

The BCEMH tablet weights decreased from 100.6 and 100.0 to 70.6 and 70.4 grams, respectively. The average dissolving rate of the BCEMH tablets was calculated to be 0.156 gram/hr.

The pH of the water in the toilet tank containing the TCCA/melamine tablets varied between 9.06 and 9.37 over 8 days of the test. The pH of water in the toilet tank containing the BCEMH tablets fluctuated between 10.0 and 9.52. The total available chlorine concentration in the water of the toilet tank containing the TCCA/melamine tablets fluctuated from 21.9 to 29.2 ppm during the test. The BCEMH tablets provide total available chlorine between 18.8 and 20.4 ppm during the test. No chlorine was detected in the headspace of either toilet tank.

Example 10

Data were generated that showed that the dissolving rate of TCCA/melamine tablets could be made to dissolve considerably slower than either the BCEMH or the 80/20 weight percent TCCA/melamine tablets by increasing the melamine content of the TCCA/melamine tablets to 30 percent weight. The water temperature during the test was 38-41°F. The data in

Figure 5 shows that the TCCA/melamine (70/30 % weight) tablets dissolved slower than the BCEMH tablets under the same test conditions.

The test data showed that the tablet weights of these TCCA/melamine tablets decreased from 100.6 and 100.4 to 86.6 and 83.2 grams, respectively during 19 days of the test.

5 The average dissolving rate of the tablets was calculated to be 0.0684 grams/hr.

The BCEMH tablet weights decreased from 102.3 and 100.4 to 60 and 56.7 grams, respectively. The average dissolving rate of the tablets was calculated to be 0.0963 grams/hr.

The pH of the water in the toilet tank containing the TCCA/melamine tablets varied between 7.75 and 9.96 over 19 days of the test. The 7.75 reading was observed in the second day
10 of the test. The pH remained above 9 after the second day. The pH of water in the toilet tank containing the BCEMH tablets fluctuated between 8.11 and 9.54.

The total available chlorine concentration in the water of the toilet tank containing the TCCA/melamine (70/30 % weight) tablets decreased from 54 to 14.5 ppm in the first 4 days the test. After that, it fluctuated from 9 to 18.7 ppm. The BCEMH tablet total available chlorine
15 decreased steadily from 33 and 8.7 ppm in the first 4 days and then fluctuated between 9.5 and 32 for the remainder of the test. Chlorine was not detected in the headspaces of either toilet tank.

Example 11

The following example demonstrates that bulking agents may be added to the water
20 treatment composition of the present invention without destroying the structural integrity of the solid form. The addition of other additives must be accomplished without effecting the chemistry between the at least one halogen source and the at least one amine compound. TCCA and melamine were blended together in a sealed glass jar to prevent exposure to humid air. The

resulting blend was subdivided and compacted into thin wafers with a diameter of about 1 inch each. The wafers were broken up with a mortar and pestle to form a granulated TCCA/melamine blend.

Other ingredients were mixed and granulated separately from the TCCA/melamine blend.

- 5 Calcium sulfate and magnesium stearate were mixed and granulated as described above. The calcium sulfate blend was then mixed with the TCCA/melamine blend and compacted into the tablets used in the following examples. This process maximizes the potential of stoichiometrical reaction between the melamine and the TCCA and is readily adapted to commercial practice.

Example 12

- 10 Calcium sulfate was added to TCCA/melamine compositions in increments of 5% and steady state dissolving rates were determined by the technique described in EXAMPLE 1. The TCCA/melamine mole ratio was maintained at approximately 3.802 in all experiments. Table III summarizes the experimental results. All ingredient amounts are in percent weights.

TABLE III

Steady State Dissolving Rates

of Tablets Comprising TCCA, Melamine and Additional Ingredients

Dissolving Rate Mg/min	Available Chlorine ppm	TCCA	Melamine	Calcium Sulfate	Magnesium Stearate
17.43	167.5	85.55	11.79	4.71	0.94
17.57	165	78.83	11.26	9.01	0.90
18.09	165	75.43	10.78	12.93	0.86
18.09	165	72.31	10.33	16.53	0.86
13.04	109.5	69.44	9.92	19.84	0.80

5 The solid form maintained its structural integrity throughout the experiments. As can be seen from the data, the dissolving rate of the water treatment compositions of the present invention can be further customized by the addition of varying amounts of metal salts such as calcium sulfate. The solid water treatment compositions of the present invention can be economically formulated by including calcium sulfate or similar bulking agents in the solid water
10 treatment compositions of the present invention.

Example 13

Data were generated to compare the average dissolving rates for TCCA tablets with those of tablets comprising about 75.43 wt % TCCA, 10.78 wt % melamine, 12.93 wt % calcium sulfate and 0.86 wt % magnesium stearate under the conditions described above in EXAMPLE
15 4. Figure 6 shows the decrease in weights of both types of tablets with time under the test conditions. The water temperature was 64-67°F during the test. The data show that the TCCA tablets dissolved faster than the TCCA/melamine tablets. For example, the weights of TCCA

tablets decreased from 100.1 and 99.9 to 72.3 and 70.9 grams, respectively over a 6 day period. The average dissolving rate of each TCCA tablet under these test conditions were calculated to be 0.193 and 0.201 grams/hour, respectively. The average dissolving rate of the two tablets was determined to be 0.197 gram/hour. The data also show that the weights of the TCCA/melamine
5 tablets decreased from 99.4 and 99.6 to 85.0 and 78.8 grams, respectively. The average dissolving rate of each tablet was determined to be 0.100 and 0.1444 gram/hour. Thus, the average dissolving rate of the two tablets was 0.1222 gram/hour.

The total available chlorine concentration in the toilet water treated with TCCA tablets was found to decrease from 75 to 8.5 ppm during the test. For the TCCA/melamine tablets, the
10 total available halogen concentration (as available chlorine) decreased from 70.8 and 12.5 ppm during the run.

The chlorine concentration in the air inside the toilet tank above the water treated with the TCCA tablets was determined to be 7.5 ppm after one day. It decreased to 1.4 ppm over the next 5 days. A strong chloramine odor was present in the toilet flushing test room. The odor became
15 overpowering when the TCCA tablets were removed each day for weighing. No chlorine was detected by the Gastec Passive Dosimeter Tubes in head space of the toilet tank containing the TCCA/melamine tablets.

Example 14

A tablet of solid water treatment composition comprising 79.20% weight TCCA, 19.80%
20 weight melamine and 0.99% weight magnesium stearate was immersed in water for 4 hours. The composition was removed from the water and a color change on the surface layer of the tablet was observed. A sample of one of the surfaces of the tablet was obtained by carefully removing a portion of the surface layer. The sample was placed in a Petri dish and dried in an oven for one

hour at 100°C. The dried material was placed in an airtight bottle until it was subjected to mass spectra analyses. FT-IR analysis was also conducted to screen compounds for functional groups.

A portion of the material was dissolved in a 50/50 mixture of reagent grade 1-pentanol and reagent grade methanol. The resulting solution was subjected to mass spectra analysis with a
5 Varian Tandem Quadropole Engine having a mass range of 1 to 850 atomic mass units (amu). The solution was scanned in the mass range of 10-400 amu. The mass spectra was then compared to the characteristics of trichloromelamine. The results indicated that the characteristics of the ions of the material obtained from the solid water treatment composition of the invention after water immersion were essentially the same as trichloromelamine (99.96%
10 certainty). The solution was then subjected to a SIM mode analysis which also matched trichloromelamine. The melting point of the material was 322.7°C, the same as trichloromelamine.

Samples of melamine and TCCA also were separately subjected to mass spectra analysis and melting point determination. The mass spectra of melamine and TCCA were nearly identical
15 to their respective mass spectra listed in the Merck MS library. The melting point of melamine was determined to be 341°C and the melting point of TCCA was determined to be 232.9°C. The results of the mass spectra analyses clearly showed halamine was formed on or near the surface layer of the solid water treatment composition after the composition was immersed in water. The results further indicate that the reaction did not occur in the interior of the solid water treatment
20 composition.

A sample was taken from the interior portion of the solid water treatment composition and subjected to the same mass spectra analyses as described above. The results of the analyses indicated that the material was essentially identical to a mixture of TCCA and melamine. The

solution was subjected to a SIM mode analysis which demonstrated that the ion species matched those of TCCA and melamine.

The present invention is not to be construed as limited in scope to the specific embodiments described herein. Indeed, various modifications of the invention in addition to
5 those described herein will become apparent to those skilled in the art from the foregoing description and accompanying figures. Such modifications are intended to fall within the scope of the appended claims.

CLAIMS

I claim:

1. A solid water treatment composition comprising at least one halogen source and at least one amine compound.
- 5 2. The solid water treatment composition of claim 1 further comprising at least one tableting additive.
3. The solid water treatment composition of claim 1 wherein said at least one halogen source comprises from about 20% to about 99% by weight and said at least one amine compound comprises from about 1% to about 80% by weight of said solid water
10 treatment composition.
4. The solid water treatment composition of claim 1 wherein said at least one halogen source composition comprises from about 30% to about 95% by weight and said at least one amine compound comprises from about 10% to about 75% by weight of said solid water treatment composition.
- 15 5. The solid water treatment composition of claim 2 wherein said at least one halogen source composition comprises from about 20% to about 85% by weight, said at least one amine compound comprises from about 10% to about 60% by weight and said at least one tableting additive comprises from about 5% to about 75% by weight of said solid water treatment composition.
- 20 6. The solid water treatment composition of claim 5 wherein said at least one halogen source composition comprises about 70% by weight, said at least one amine compound comprises about 10% by weight and said at least one tableting additive comprises about 20% by weight of said solid water treatment composition.

7. The solid water treatment composition of claim 2 wherein the at least one halogen source comprises from about 1% to about 10% by weight, the at least one amine compound comprises from about 1% to about 10% by weight and the at least one tableting additive comprises about 90% by weight of said solid water treatment composition.
8. The solid water treatment composition of claim 1 wherein said at least one halogen source provides a halogen selected from the group consisting of chlorine, bromine and iodine or combinations thereof.
9. The solid water treatment composition of claim 8 wherein said at least one halogen source provides a chlorine.
10. The solid water treatment composition of claim 8 wherein said at least one halogen source provides a bromine.
11. The solid water treatment composition of claim 1 wherein said at least one halogen source comprises a member selected from the group consisting of trichloroisocyanuric acid, dichloroisocyanuric acid, monochloroisocyanuric acid, potassium dichloroisocyanuric acid, anhydrous sodium dichloroisocyanuric acid, sodium dichloroisocyanuric dihydrate, tribromoisocyanuric acid, monobromoisocyanuric acid, dibromoisocyanuric acid, bromo-chloroisocyanuric acid derivatives, 1,3-dichloro-5,5-dimethyl-hydantoin, 1,3-dibromo -5,5dimethyl-hydantoin, 1-3-chloro-5,5-dimethyl-hydantoin, 1 bromo,3-chloro-5,5-dimethyl-hydantoin, 1,3-dichloro-5-methyl-5-ethylhydantoin, trichloromelamine, dichloromelamine, monochloromelamine, hexachloromelamine, tribromomelamine, dibromomelamine, monobromelamine, calcium hypochlorite, lithium hypochlorite, and combinations

thereof.

12. The solid water treatment composition of claim 1 wherein said at least one halogen source comprises a member selected from the group consisting of a composition comprising one mole trichloroisocyanuric acid and four moles potassium
5 dichloroisocyanuric acid; a composition comprising sodium bromide and chlorine; a composition comprising potassium bromide and chlorine; a composition comprising a metal bromide and chlorine; and a composition comprising trichloroisocyanuric acid and potassium bromide.
13. The solid water treatment composition of claim 1 wherein said halogen source
10 comprises trichloroisocyanuric acid.
14. The solid water treatment composition of claim 1 wherein said halogen source comprises about 60% by weight 1-bromo-3-chloro-dimethyl hydantoin, about 30% by weight 1,3 dichloro 5,5 dimethyl hydantoin and about 10% by weight 1,3-dichloro-5-ethyl, 5-methyl hydantoin based on the weight of the at least one halogen
15 source.
15. The solid water treatment composition of claim 1 wherein said at least one amine compound comprises an unhalogenated amine.
16. The solid water treatment composition of claim 1 wherein said at least one amine compound comprises an aromatic amine.
- 20 17. The solid water treatment composition of claim 1 wherein said at least one amine compound comprises a heterocyclic amine.
18. The solid water treatment composition of claim 1 wherein said at least one amine compound is selected from the group consisting of melamine and derivatives thereof,

pyrimidine derivatives, piperazine and derivatives thereof, piperidine derivatives, piperidone derivatives, piperazine diones and derivatives thereof, pyridine derivatives, pyridazine and derivatives thereof, naphthyridines derivatives, anthracene derivatives, hydantoin derivatives, imidazole derivatives, imidazolidinone derivatives, glycoluril derivatives, oxazolidinone derivatives and combinations or mixtures thereof.

19. The solid water treatment composition of claim 1 wherein said at least one amine compound comprises melamine.

20. The solid water treatment composition of claim 2 wherein said tableting additive comprises calcium sulfate.

21. The solid water treatment composition of claim 2 comprising about 70% by weight trichloroisocyanuric acid, about 10% by weight melamine and about 20% calcium sulfate, based on the weight of said solid water treatment composition.

22. The solid water treatment composition of claim 2 wherein said solid water treatment composition measures at least 1/4" thick and at least 1/2" in diameter.

23. The solid water treatment composition of claim 22 wherein said water treatment composition measures at least 3" thick and at least 4" in diameter.

24. The solid water treatment composition of claim 2 wherein said solid water treatment composition weighs at least 5 grams.

25. The solid water treatment composition of claim 1 in the form of a unitary compacted tablet.

26. The solid water treatment composition of claim 2 in the form of a plurality of discrete granules.

27. The solid water treatment of claim 26 wherein each of said discreet granules contains at least one halogen source, at least one amine compound, and at least one tableting additive.
28. The solid water treatment composition of claim 26 wherein at least some granules contain of at least one halogen source and at least one amine compound but no tableting additives.
29. The solid water treatment composition of claim 28, further comprising granules containing at least one tableting additive but no halogen source or amine compound.
30. The solid water treatment composition of claim 1 in the form of a powder.
31. A method of producing a solid water treatment composition comprising admixing at least one halogen source and at least one amine compound.
32. The method of claim 31 further comprising admixing at least one tableting additive with the at least one halogen source and at least one amine compound.
33. The method of claim 31 wherein said admixture is compressed into a solid form by applying an effective amount of pressure.
34. The method of claim 31 wherein said at least one halogen source comprises from about 20% to about 99% by weight and said at least one amine compound comprises from about 1% to about 80% by weight of said solid water treatment composition.
35. The method of claim 32 wherein said at least one halogen source comprises from about 30% to about 95% percent weight and said at least one amine compound comprises from about 10% to about 75% by weight based on the weight of said solid water treatment composition.
36. The method of claim 35 wherein said at least one halogen source composition

comprises from about 20% to about 85% by weight, said at least one amine compound comprises from about 10% to about 60% by weight and said tableting additive comprises from about 5% to about 75% by weight based on the weight of said solid water treatment composition.

5 37. The method of claim of claim 36 wherein said at least one halogen source composition comprises about 70% by weight, said at least one amine compound comprises about 10% by weight and said tableting additive comprises about 20% by weight of solid water treatment composition based on the weight of said solid water treatment composition.

10 38. The method of claim 34 wherein the at least one halogen source comprised from 1% to 10% by weight, the at least one amine compound comprises from 1% to 10% by weight and the tableting additive comprises about 90% by weight based on the weight of said solid water treatment composition.

15 39. The method of claim 31 wherein said at least one halogen source provides a halogen selected from the group consisting of chlorine, bromine and iodine or combinations thereof.

40. The method of claim 39 wherein said at least one halogen source comprises a chlorine.

20 41. The method of claim 39 wherein said at least one halogen source comprises a bromine.

42. The method of claim 31 wherein said at least one halogen source comprises a member selected from the group consisting of trichloroisocyanuric acid, dichloroisocyanuric acid, monochloroisocyanuric acid, potassium dichloroisocyanuric

acid, anhydrous sodium dichloroisocyanuric acid, sodium dichloroisocyanuric dihydrate, tribromoisocyanuric acid, monobromoisocyanuric acid, dibromoisocyanuric acid, bromo-chloroisocyanuric acid derivatives, 1,3-dichloro-5,5-dimethyl-hydantoin, 1,3-dibromo -5,5-dimethyl-hydantoin, 1-2-chloro-5,5-dimethyl-hydantoin, 1 bromo,3-chloro-5,5-dimethyl-hydantoin, 1,3-dichloro-5-methyl-5-ethylhydantoin, trichloromelamine, dichloromelamine, monochloromelamine, hexachloromelamine, tribromomelamine, dibromomelamine, monobromomelamine, calcium hypochlorite, lithium hypochlorite, and combinations thereof.

43. The method of claim 31 wherein said at least one halogen source comprises a member selected from the group consisting of a composition comprising one mole trichloroisocyanuric acid and four moles potassium dichloroisocyanuric acid; a composition comprising sodium bromide and a chlorine; a composition comprising potassium bromide and chlorine; a composition comprising a metal bromide and chlorine; and a composition comprising trichloroisocyanuric acid and potassium bromide.

44. The method of claim 31 wherein said halogen source comprises trichloroisocyanuric acid.

45. The method of claim 31 wherein said halogen source comprises about 60% by weight 1-bromo-3-chloro-dimethyl hydantoin, about 30% by weight dichloro-dimethyl hydantoin and about 10% by weight 1,3-dichloro-5-ethyl, 5-methyl hydantoin.

46. The method of claim 31 wherein said at least one amine compound comprises an unhalogenated amine.

47. The method of claim 31 wherein said at least one amine compound comprises an aromatic amine.
48. The method of claim 31 wherein said at least one amine compound comprises a heterocyclic amine.
- 5 49. The method of claim 31 wherein said at least one amine compound is selected from the group consisting of melamine and derivatives thereof, pyrimidine derivatives, piperazine and derivatives thereof, piperidine derivatives, piperidone derivatives, piperazine diones and derivatives thereof, pyridine derivatives, pyridazine and derivatives thereof, naphthyridines derivatives, anthracene derivatives, hydantoin derivatives, imidazole derivatives, imidazolidinone derivatives, glycoluril derivatives, 10 oxazolidinone derivatives and combinations or mixtures thereof.
50. The method of claim 31 wherein said at least one amine compound comprises melamine.
51. The method of claim 32 wherein said tableting additive is calcium sulfate.
- 15 52. The method of claim 32 wherein said halogen source comprises about 70% by weight trichloroisocyanuric acid, said at least one unhalogenated amine compound comprises about 10% by weight melamine and said tableting additive comprises about 20% calcium sulfate.
53. The method of claim 32 wherein said admixture is formed by providing a first portion 20 comprising at least one halogen source and at least one amine compound, providing a second portion comprising at least one tableting additive and combining said first portion and said second portion.
54. The method of claim 33 wherein said particles are about 99% greater than 60 mesh

and about 1% no greater than 12 mesh prior to applying said pressure to said admixture.

5 55. The method of claim 53 wherein the admixture is formed by applying pressure to said first portion and said second portion in an amount effective to form a first flat solid composition, breaking said first flat solid composition into particles having a particle distribution about 99% greater than 60 mesh and about 1% no greater than 12 mesh.

56. The method of 55 wherein said admixture is compressed into a compacted tablet by applying an effective amount of pressure.

10 57. A method of disinfecting and controlling biofouling of a water system comprising introducing into water of the water system an effective amount of solid water treatment composition according to claim 1

58. The method of claim 57 comprising introducing into the water a solid water treatment composition according to claim 2.

15 59. The method of claim 57 comprising introducing into the water a solid water treatment composition according to claim 3.

60. The method of claim 57 comprising introducing into the water a solid water treatment composition according to claim 4.

20 61. The method of claim 58 comprising introducing into the water a solid water treatment composition according to claim 5.

62. The method of claim 58 comprising introducing into the water a solid water treatment composition according to claim 6.

63. The method of claim 57 comprising introducing into the water the solid water

treatment composition according to claim 7.

64. The method of claim 57 comprising introducing into the water a solid water treatment composition according to claim 8.

5 65. The method of claim 57 wherein comprising introducing into the water a solid water treatment composition according to claim 21.

66. The method of claim 57 wherein said solid water treatment composition according to claim 1 is introduced into the water by placing said solid water treatment composition in direct contact with water.

10 67. The method of claim 59 wherein said solid water treatment composition according to claim 1 is introduced into the water by placing said solid water treatment composition in a holding device and then placing said solid water treatment composition in direct contact with water.

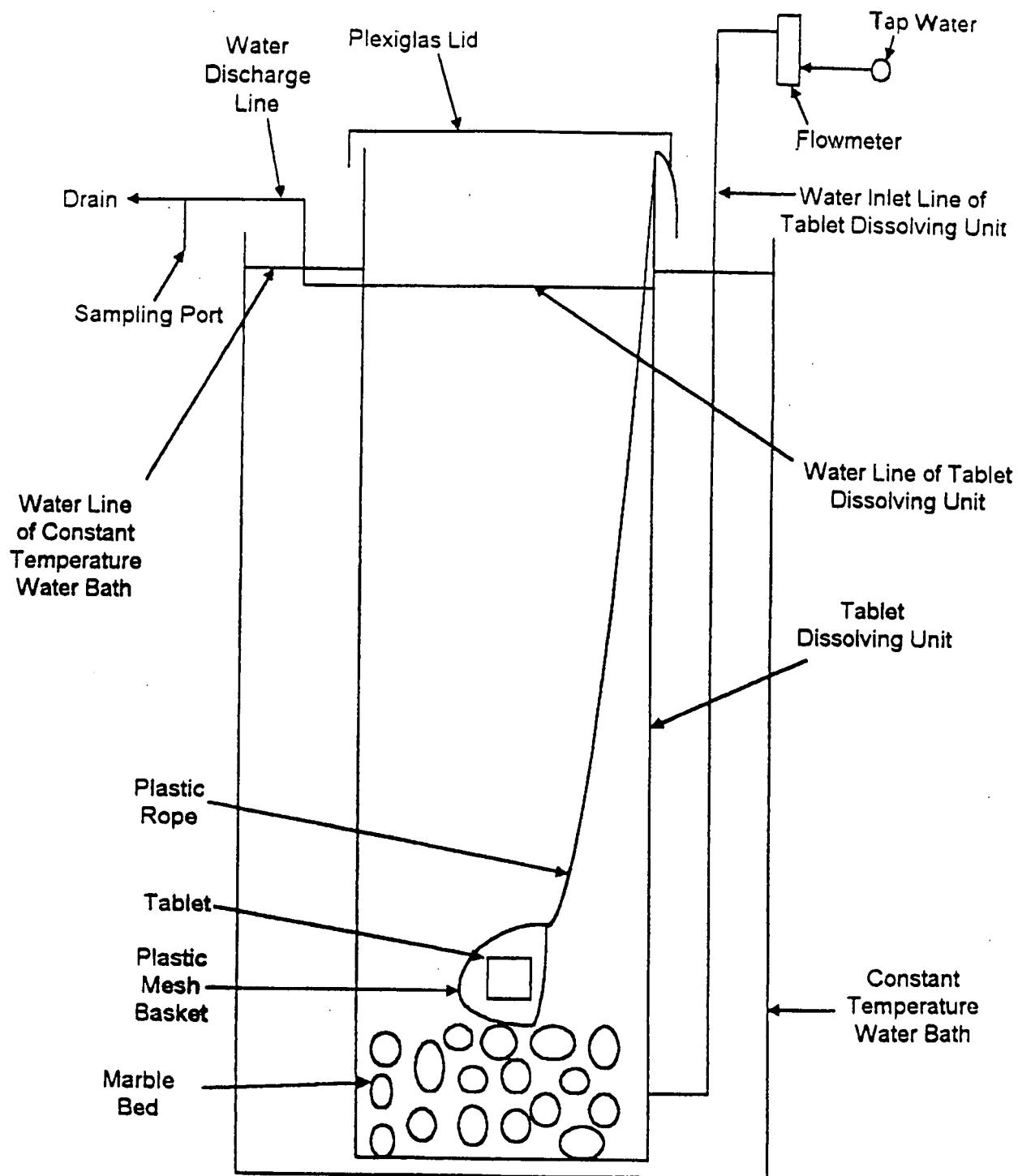


Figure 1.

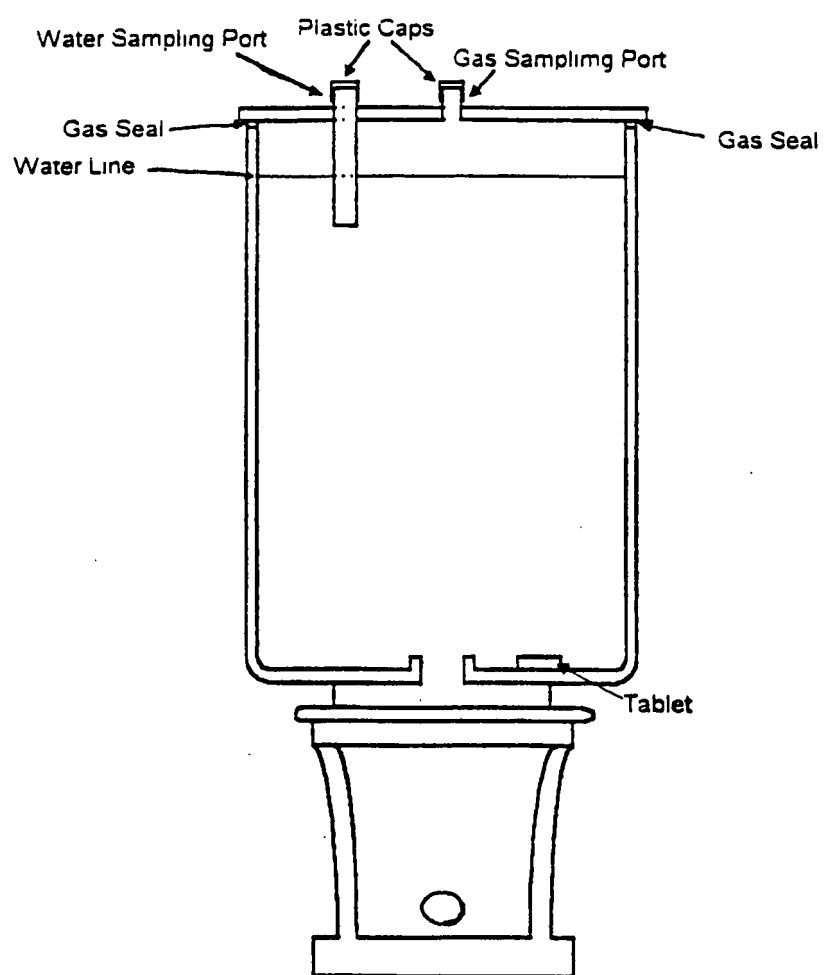


Figure 2.

Figure 3.

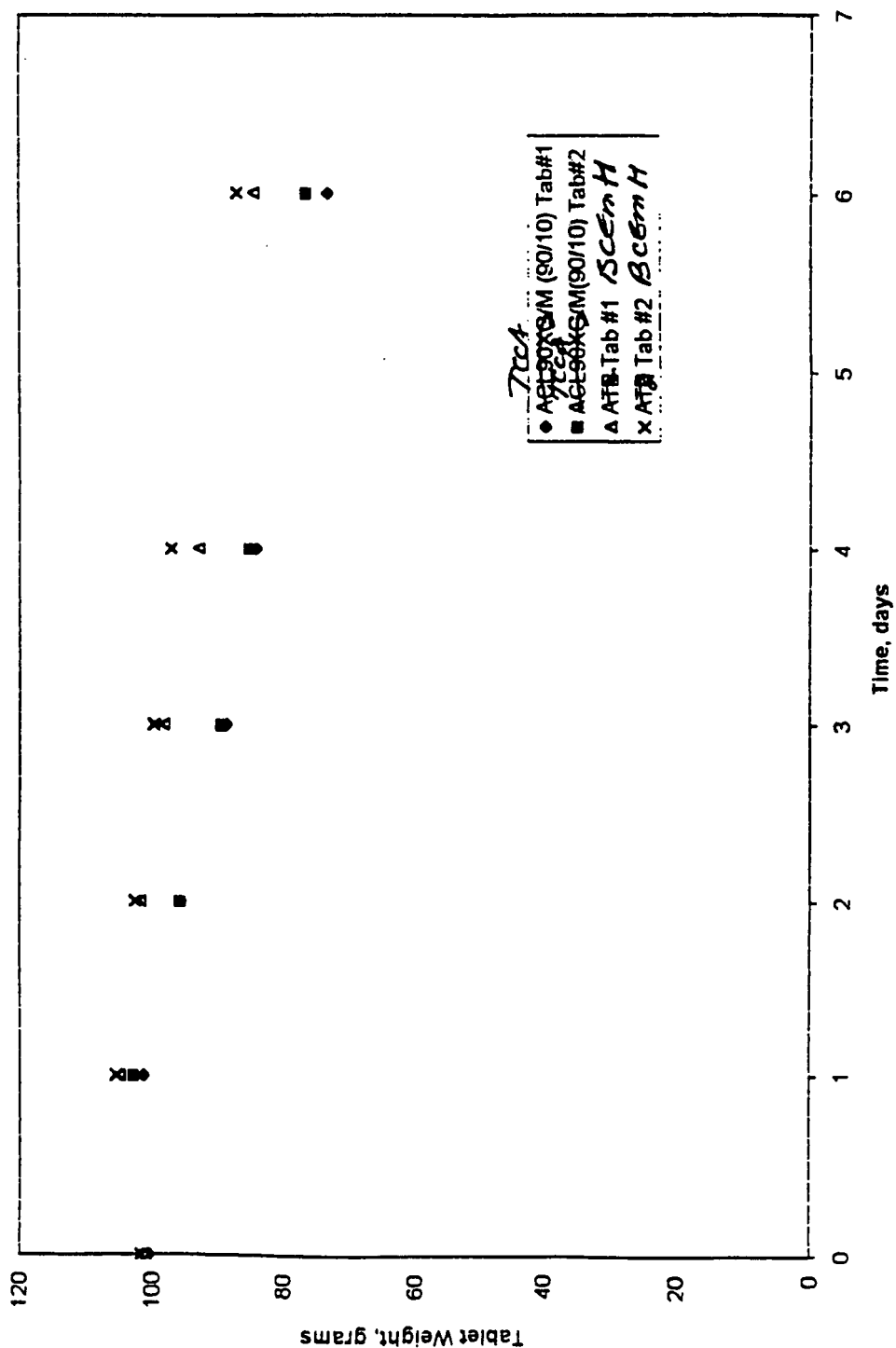


Figure 4.

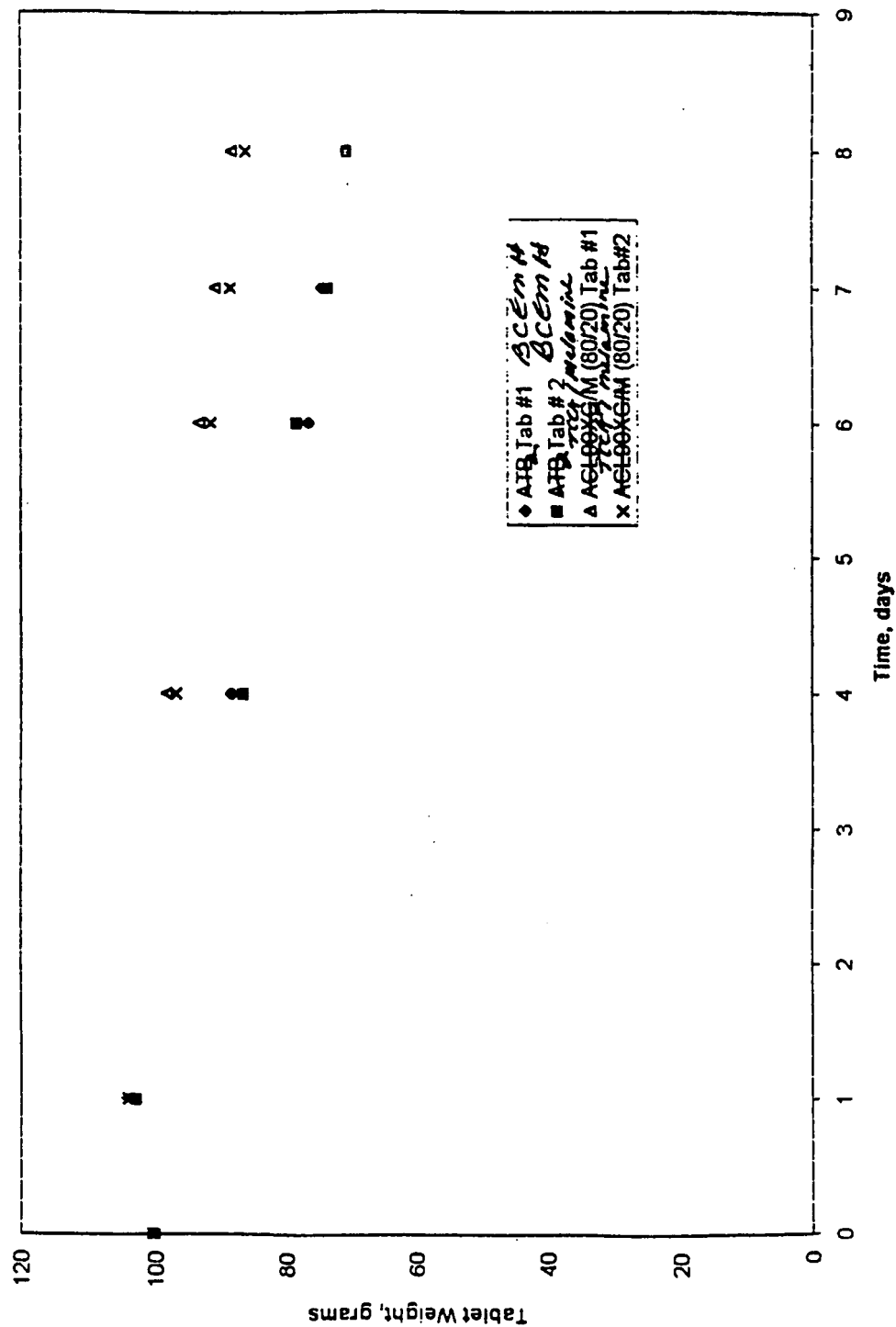
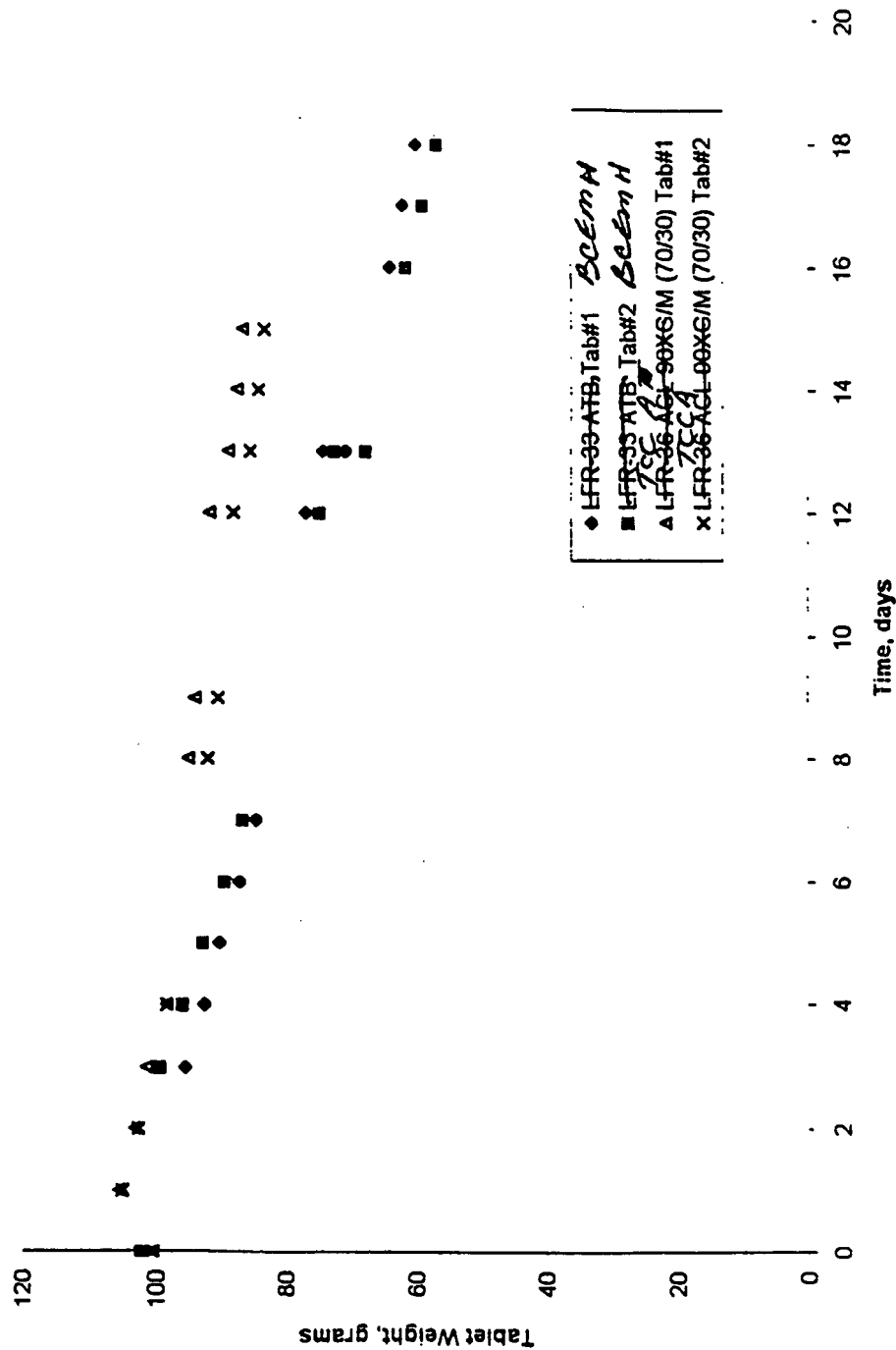


Figure 5.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/27861

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F1/76 C02F1/00 C02F1/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 92 13528 A (BIO-LABS) 20 August 1992 (1992-08-20)</p> <p>page 8, line 1-7; claims 1-16 --- -/--</p>	<p>1-5, 8-10, 15, 17, 18, 25-28, 30-32, 34-36, 39-41, 46, 48, 49, 53, 57-61, 65-67</p>

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

29 March 2000

Date of mailing of the international search report

07/04/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.

Authorized officer

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/27861

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 0 403 465 A (UNIVERSITY OF HOUSTON) 19 December 1990 (1990-12-19)</p> <p>claims 1-47</p>	<p>1-3, 8-13, 15, 17, 18, 25-28, 30-32, 34, 35, 39-44, 46, 48, 49, 53, 57-59, 64, 66, 67</p>
X	<p>WO 93 04987 A (MONSANTO COMPANY) 18 March 1993 (1993-03-18)</p> <p>page 6, line 6 - line 30; claims 1-6</p>	<p>1-3, 8-11, 15, 17, 18, 25</p>
X	<p>WO 96 36224 A (BIO-LABS) 21 November 1996 (1996-11-21)</p> <p>page 7, line 16; claims 1-29</p>	<p>1-4, 8, 9, 15, 17, 18, 25-27, 31, 32, 34, 35, 39, 40, 46, 48, 49, 57-60, 64, 66</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/27861

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9213528 A	20-08-1992	AU 651186 B	14-07-1994
		AU 1419492 A	07-09-1992
		CA 2103715 A,C	12-08-1992
		EP 0571523 A	01-12-1993
		JP 7506330 T	13-07-1995
		MX 9200563 A	01-08-1992
		PT 100112 A,B	30-06-1993
		US 5498415 A	12-03-1996
		ZA 9200798 A	25-11-1992
EP 403465 A	19-12-1990	AT 92012 T	15-08-1993
		AU 640153 B	19-08-1993
		AU 5924890 A	08-01-1991
		CA 2056379 A	17-12-1990
		DE 69002442 T	13-07-1995
		DK 429631 T	30-08-1993
		EP 0429631 A	05-06-1991
		ES 2044603 T	01-01-1994
		IL 94743 A	19-01-1996
		MX 173274 B	14-02-1994
		WO 9015780 A	27-12-1990
		US 5464636 A	07-11-1995
		US 5476670 A	19-12-1995
		US 5688515 A	18-11-1997
		US 5527547 A	18-06-1996
		US 5662940 A	02-09-1997
WO 9304987 A	18-03-1993	AU 2479692 A	05-04-1993
		MX 9204952 A	01-03-1993
		US 5688515 A	18-11-1997
WO 9636224 A	21-11-1996	US 5648314 A	15-07-1997
		AU 706731 B	24-06-1999
		AU 5738896 A	29-11-1996
		CA 2221252 A	21-11-1996

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C02F 1/76, 1/50, 5/08	A1	(11) International Publication Number: WO 90/15780 (43) International Publication Date: 27 December 1990 (27.12.90)
(21) International Application Number: PCT/US90/03139 (22) International Filing Date: 4 June 1990 (04.06.90) (30) Priority data: 366,936 16 June 1989 (16.06.89) US (71) Applicant: UNIVERSITY OF HOUSTON [US/US]; 4800 Calhoun, Houston, TX 77204-4791 (US). (72) Inventors: RAKESTRAW, Lawrence, Frederick ; 15844 Country Ridge Drive, Chesterfield, MO 63017 (US). MATSON, Jack, Vincent ; 10919 Braes Forest, Houston, TX 77071 (US). ZHANG, Zhihe ; 6310 Rampart, No. 28, Houston, TX 77081 (US). HIGHT, Terry Van Temple ; 6202 Creekbend, Houston, TX 77096 (US). KUECHLER, Thomas, C.; 702 Montmartre, St. Louis, MO 63141 (US).		(74) Agent: COLE, Arnold, Harvey; Monsanto Company, 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US). (81) Designated States: AT (European patent), AU, BE (European patent), BG, BR, CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, RO, SE (European patent), SU. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: BIOCIDAL METHODS AND COMPOSITIONS FOR RECIRCULATING WATER SYSTEMS (57) Abstract Improved biocidal composition and method for controlling biofouling and microorganism population levels in recirculating water systems such as cooling towers, swimming pools or spas is disclosed and claimed. The composition comprises a hypochlorite donor and a bromide ion donor in proportions selected to maintain a mole ratio of the sum of all bromine containing species to the sum of all hypohalite species in the recirculating water of about 0.2 to about 20. The method comprises introducing into the recirculating water a mixture or combination of a hypochlorite donor and a bromide ion donor in an amount sufficient to maintain a ratio of the sum of all bromine containing species to the sum of all species in the recirculating water in the range of about 0.2 to about 20. In addition, a bromine volatilization suppressant may be introduced into the recirculating water to inhibit loss of bromide ion through volatilization of bromine containing species formed by reaction of the hypochlorite donor and the bromide ion donor. One or more scale inhibitors and compacting aids may also be added.		

DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MC	Monaco
AU	Australia	FI	Finland	MG	Madagascar
BB	Barbados	FR	France	ML	Mali
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GR	Greece	NL	Netherlands
BJ	Benin	HU	Hungary	NO	Norway
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	SD	Sudan
CF	Central African Republic	KP	Democratic People's Republic of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SN	Senegal
CH	Switzerland	LI	Licchtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
DE	Germany, Federal Republic of	LU	Luxembourg	TC	Togo
DK	Denmark			US	United States of America

-1-

BIOCIDAL METHODS AND COMPOSITIONS FOR RECIRCULATING WATER SYSTEMSBACKGROUND OF THE INVENTION1. Field of the Invention

5 This invention relates to the disinfection of water and to the control of biofouling in recirculating water systems such as cooling towers, evaporative condensers, air washers, swimming pools, hot tubs, and spas.

10 The invention more especially concerns methods and compositions for controlling biofouling and microorganism population levels in such systems wherein water soluble hypochlorite donors and bromide ion donors are added to the systems so as to improve biocidal effectiveness with
15 reduced costs.

As used herein, the term "hypochlorite donor" means any compound that will generate hypochlorite species when dissolved in water.

20

The term "bromide ion donor" means any compound that will generate bromide ions when dissolved in water.

25 The term "available halogen" means the standard form for expressing the strengths or capacities of halogenating chemicals as well as for the doses in which they are applied and for the hypohalite species (HOCl , OCl^- , HOBr , OBr^-) which remain in the water.

30 The term "available chlorine" means the same as "available halogen", but refers specifically to chlorine compounds.

35 The term "available bromine" means the same as "available halogen", but refers specifically to bromine compounds.

-2-

The term "hypohalite species" means hypochlorous acid, hypochlorite ion, hypobromous acid and hypobromite ion.

- 5 The term "hypochlorite species" means hypochlorous acid and hypochlorite ion.

The term "hypobromite species" means hypobromous acid and hypobromite ion.

10.

The term "bromine species" means hypobromous acid, hypobromite ion, and bromide ion.

- 15 The terms "free halogen" and "free available halogen" are used interchangeably and are defined as the concentration of halogen existing in the water as hypohalous acid, HOX, and hypohalite ion, OX^- , where X is Cl or Br.

- 20 The terms "free chlorine" and "free available chlorine" are used interchangeably and are defined as the concentration of chlorine existing in the water as hypochlorous acid, HOCl, and hypochlorite ion, OCl^- .

- 25 The terms "free bromine" and "free available bromine" are used interchangeably and are defined as the concentration of bromine existing in the water as hypobromous acid, HOBr, and hypobromite ion, OBr^- .

- 30 The terms "combined halogen" and "combined available halogen" are used interchangeably and are defined as the concentration of halogen existing in the water in chemical combination with ammonia or organic nitrogen compounds.

- 35 The terms "combined chlorine" and "combined available chlorine" are used interchangeably and are defined as the

-3-

concentration of chlorine existing in the water in chemical combination with ammonia or organic nitrogen compounds.

- 5 The terms "combined bromine" and "combined available bromine" are used interchangeably and are defined as the concentration of bromine existing in the water in chemical combination with ammonia or organic nitrogen compounds.
- 10 The terms "total halogen" and "total available halogen" are used interchangeably and are defined as the sum of "free halogen" (or "free available halogen") and "combined halogen" (or "combined available halogen").
- 15 The terms "total chlorine" and "total available chlorine" are used interchangeably and mean the same as "total halogen" and "total available halogen" but specifically refer to chlorine.
- 20 The terms "total bromine or "total available bromine" are used interchangeably and mean the same as "total halogen" and "total available halogen" but specifically refer to bromine.
- 25 The symbol "FAvC" represents "free chlorine" and "free available chlorine" concentrations in the water.
- The symbol "AvC" represents the available chlorine content of the hypochlorite donor.
- 30 The term "halogen demand" is defined as the amount of halogen which must be added to the water over a specific period of time to maintain the "free halogen" and/or "free available halogen" at a specific concentration in the
- 35 water.

-4-

The term "chlorine demand" means the same as the "halogen demand" but specifically refers to "free chlorine" and/or "free available chlorine" concentrations.

5 The term "chlorinated isocyanuric acid derivative" means chlorinated isocyanuric acid including dichlorinated and trichlorinated isocyanuric acid, alkali metal and alkaline earth metal salts of chlorinated isocyanuric acid, and hydrates, complexes and mixtures thereof.

10

The term "hydantoin derivative" means an unsubstituted, halogenated (i.e. chlorinated or brominated), or alkylated hydantoin.

15 The term "sulfamic acid derivative" means unsubstituted, halogenated, or alkylated sulfamic acid.

The term "sulfonamide derivative" means halogenated, alkylated, or arylated sulfonamide.

20

The term "glycoluril derivative" means unsubstituted, halogenated, or alkylated glycoluril.

25 The term "succinimide derivative" means unsubstituted, halogenated, or alkylated succinimide.

The term "oxazolidinone derivative" means an unsubstituted, halogenated, alkylated, or arylated oxazolidinone.

30

The term "imidazolidinone derivative" means an unsubstituted, halogenated, alkylated, or arylated imidazolidinone.

35 The term "halogen concentration (free chlorine basis or free available chlorine basis)" means the halogen

-5-

concentration in terms of free available chlorine, regardless of whether the halogen species are hypochlorite, hypobromite or mixtures thereof.

5 2. Related Art

Cooling towers are used to provide cooling for the air conditioning systems of office buildings, hotels and hospitals and to provide cooling for industrial processes.

10 The water in these towers is subject to contamination from the air blown through the tower and from the fresh water used to compensate for evaporative losses and blowdown. The contamination consists of both inorganic and organic debris as well as live microorganisms capable of growing

15 and multiplying if suitable conditions are provided. Formation of microbial deposits, known as biofouling, can occur on almost any surface exposed to an aqueous environment, causing substantial energy losses due to increased heat transfer resistance. For this and other

20 reasons, cooling towers are adversely affected by microorganisms, e.g. bacteria, fungi, molds, and algae, by either sheer numbers of organisms, metabolic waste products generated, health hazards presented, or deposits created. Unfortunately, cooling towers provide many of

25 the conditions ideal for microbial growth, namely favorable temperatures and moisture levels, and favorable concentrations of air and nutrients.

Air washers are used to cool, cleanse, and humidify

30 the air in office buildings, factories, shopping malls, and the like. Due to the large amount of air drawn through the water, the growth of microorganisms is again a problem. Since the air is used directly for inhabited areas, the toxicity and odor of any compounds used for

35 treatment of the water in the air washers must be extremely low.

-6-

Similarly, water in swimming pools, hot tubs and spas must be sanitized in order to control disease spreading microorganisms. As with air washers, the toxicity and odor of compounds used to treat the water must be
5 extremely low.

It is customary to treat biologically contaminated water with one or more biocides to control the population of microorganisms in the water, to prevent fouling of heat
10 exchanger surfaces, and to prevent the spread of disease. The biocides most commonly used to disinfect and sanitize water in recirculating water systems are chemicals that generate hypochlorite species when dissolved in water. There are many hypochlorite generating chemicals, but the
15 more common ones are chlorine gas, alkali metal hypochlorites such as sodium hypochlorite, alkaline earth metal hypochlorites such as calcium hypochlorite, chlorinated hydantoins, and chlorinated isocyanuric acid derivatives.

20

Dry sources of biocide are often preferable to gaseous or even liquid forms because the dry forms are often safer to handle, more convenient to store and use, and more stable in storage. Moreover, one or more dry
25 products may conveniently be fed to a recirculating water system using an erosion feeder in which water is passed through a bed of solid biocide to slowly dissolve the biocide and is then added to the recirculating water. One such erosion feeder is described in U.S. Patent 3,412,021.

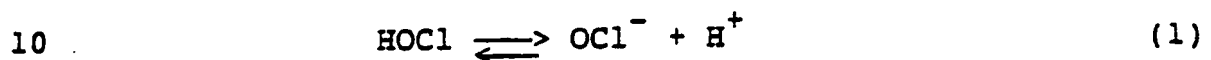
30

The different forms of hypochlorite donors all work by generating hypochlorous acid (HOCl) in solution, which provides the significant biocidal action. Hypochlorous acid has strong biocidal properties under the proper
35 conditions. Its killing power is adversely affected,

-7-

however, by alkaline pH levels and by the presence of ammonia or other nitrogenous material.

The pH of cooling water is typically regulated in the range of 8.0 to 9.0 for alkaline corrosion protection. At pH levels above 7.5, chlorine-based biocides become less effective because of the equilibrium shift from hypochlorous acid to hypochlorite ion.



$$\text{pK} = -\log \left[\frac{[\text{OCl}^-][\text{H}^+]}{[\text{HOCl}]} \right] = 7.5 \text{ (at } 20^\circ\text{C)}$$

The hypochlorite ion cannot easily penetrate microorganism cell membranes, while the uncharged hypochlorous acid can passively diffuse into cells to cause damage.

Water in recirculating water systems is also frequently contaminated with ammonia due to the decomposition of nitrogenous impurities in the water or to the leakage of ammonia from refrigeration units into the cooling water. Ammonia or chloramines are also commonly introduced into the recirculating water system by the makeup water. Hypochlorite species react with ammonia to form chloramines. Since chlorine is bound very strongly by nitrogen, the chlorine is not readily released by chloramines to the water as hypochlorite species, and the biocidal activity of the chlorine-based biocide is, therefore, greatly reduced. The fact that the chloramines are relatively stable chlorine compounds also makes it more difficult for some cooling tower systems to comply with the EPA total halogen (free halogen + combined halogen) discharge limit of 0.2 ppm. In some cases, these cooling tower systems frequently have to dechlorinate the discharge water in order to be in compliance. Moreover, chloramines have a disagreeable and irritating odor. They

-8-

can be converted to odorless nitrogen gas by maintaining the appropriate free chlorine concentration in the recirculating water, but some chloramines are still volatilized into the air. Even though the amounts are negligible, chloramine odors are still noticeable. Chloramine odor is an important issue with indoor pools and spas because the air containing the volatilized chloramines is retained in the buildings long enough for the chloramine concentration to accumulate to levels that are objectionable to the consumer. Thus, the formation of chloramines in recirculating water can present a serious obstacle to the use of chlorine-based biocides.

Hypobromous acid (HOBr), which can be generated from a number of compounds including liquid bromine and N-bromo organic compounds or by reacting a bromide salt with a solution of hypochlorous acid or other oxidizing agents, is a more effective biocide on a molar basis than hypochlorous acid. Under some conditions, this superiority is quite dramatic. In particular, hypobromous acid is known to react with ammonia to produce bromamines. Bromamines, unlike chloramines, have very good biocidal activity and have a more acceptable odor. Bromamines also have a distinct advantage over chloramines because they dissipate more readily, thereby making it easier to operate cooling towers in compliance with the EPA limits for total halogen. In addition, hypobromite species are more effective than hypochlorite species at pH values above 7.5 due to the higher pK value for the equilibrium shift from hypobromous acid to hypobromite ion.

-9-



$$\text{pK} = -\log \left[\frac{[\text{OBr}^-][\text{H}^+]}{[\text{HOBr}]} \right] = 8.5 \text{ (at } 20^\circ\text{C)}$$

5 In most cases where hypobromous acid is used as a biocidal agent, the hypobromous acid generating composition contains a large weight percentage of bromine. Liquid bromine, for example, is 100% bromine by weight and 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH) is 32.8% bromine by weight. This practice leads to higher costs for the bromine-based biocides since the cost of bromine is about three times the cost of chlorine per pound. 15 Since 2.25 pounds of bromine contain the same number of moles of available halogen as only 1.0 pound of chlorine, bromine is over seven times more expensive than chlorine on a per mole basis. Even though hypobromous acid is generally superior to hypochlorous acid, the higher cost 20 of bromine has limited the use of bromine-based biocides.

Nevertheless, in the past few years several products have been introduced into the cooling tower marketplace which take advantage of the bromine chemistry. In 1982, 25 Nalco introduced a bromine-based product (tradename Actibrom) for use in large scale cooling towers. These towers already had chlorinators injecting gaseous chlorine for disinfection. Actibrom is simply an aqueous solution of sodium bromide, and is typically added in proportion to 30 the chlorine gas using a separate feeder. See U.S. Patent No. 4,451,376. Another bromine-based biocide, 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH) was introduced into the cooling tower marketplace by Great Lakes Chemical. See U.S. Patent No. 4,297,224.

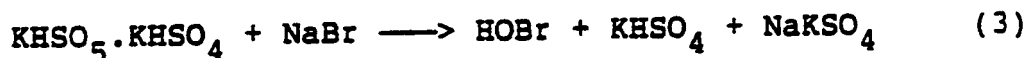
35

Bromine sanitizers have also gained some measure of popularity for indoor pool and spa applications, because the odor of the bromamines, formed by reaction of

-10-

hypobromite species with nitrogenous wastes, is less objectionable to the consumer. Bromine sanitizers, however, have not been popular for outdoor pools because the hypobromite species are rapidly dissipated in sunlight and the sanitizer costs are considerably higher than chlorine sanitizers with cyanuric acid.

Potassium monopersulfate and sodium bromide have been marketed together as a bromine sanitizer system for spa applications. The recommended practice is to dose the spa water with sodium bromide (usually as a solution) and then add the recommended dosages of potassium monopersulfate as needed. Hypobromous acid is generated by oxidation of the bromide ion with persulfate ions as shown by the following equation:

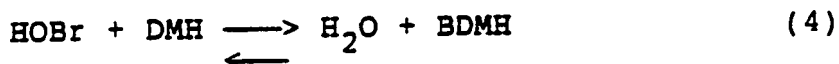


Currently available dry sources of hypobromous acid suffer from a number of disadvantages in addition to their higher cost. The hydantoin products such as BCDMH, 1,3-dichloro-5,5-dimethylhydantoin (CCDMH), 1,3-dibromo-5,5-dimethylhydantoin (BDDMH), 1,3-dichloro-5-ethyl-5-methylhydantoin (CCEMH), and 1-bromo-3-chloro-5-ethyl-5-methylhydantoin (BCEMH) have very low dissolution rates which necessitates the use of large feeder systems and high water flow rates. Moreover, in some cases it is desirable to add a large amount of available halogen at one time to rapidly clean up a recirculating water system. This is known as a "shock treatment". Such a treatment would be desired whenever a system has experienced a large amount of contamination or when microorganism growth has gotten out of control. However, the hydantoin products are generally unsuited for this application due to their low dissolution rates.

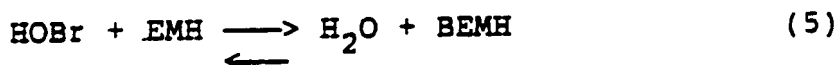
-11-

In addition, the hydantoin products are not as effective biocides as might be expected based on the amount of hypobromous acid formed, because these products also release large amounts of 5,5-dimethylhydantoin (DMH) or 5-ethyl-5-methylhydantoin (EMH) into the water, eventually leading to the buildup of high concentrations of DMH or EMH in the water. High concentrations of DMH or EMH inhibit the biocidal activity of the hypobromous acid by virtue of the following equilibria:

10



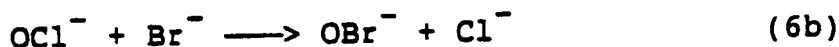
15



where BDMH is bromo-DMH and BEMH is bromo-EMH. This effect has previously been noted in U.S. Patent 4,698,165.

As an alternative to the hydantoins, hypobromous acid may be prepared by reacting a bromide salt with a source of hypochlorite species according to the following equation:

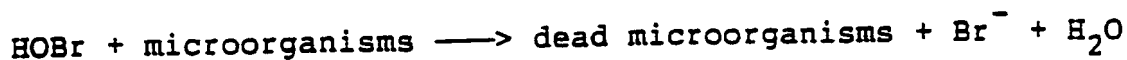
25



as previously taught, for example, in British Patent 1,327,531 and U.S. Patents 2,815,311; 3,975,271; and 4,119,535. The hypobromous acid formed by the above equation is the active biocide. However, in the process of killing microorganisms or oxidizing organic material, the hypobromous acid is reduced to form bromide ion, as shown by the following equation:

-12-

(7)



Thus, the bromide ion can be reused to generate more hypobromous acid by reaction with hypochlorite species as shown above in equations 6a and 6b. Because the bromide ion is continuously reused, only small amounts of bromide ion are necessary to make a chlorine-based biocide in combination with bromide salts perform as a bromine biocide.

Some prior art teaches that, when using mixtures of chlorine-based biocides in combination with bromide salts large excesses of bromide ion should be maintained in the recirculating water. For example, British Patent No. 1,327,531 describes a process for sanitizing swimming pool water wherein the concentration of bromide is maintained at 20 to 50 mg per liter (expressed as sodium bromide) and the concentration of the hypobromite species is maintained at 0.4 mg/L. Other prior art, e.g., U.S. Patent No. 3,975,271, suggests that when hypobromous acid is generated by reacting a bromide salt with a source of hypochlorous acid, the optimum mole ratio of chlorine to bromide is near 1. However, no information is provided as to how to maintain the ratio near the optimum in the recirculating water while chlorine and bromide salts are being fed simultaneously to the system as well as being lost from the system.

30

SUMMARY OF THE INVENTION

This invention is broadly concerned with compositions and methods for controlling biofouling and microorganism population levels in recirculating water systems using compositions or combinations of hypochlorite donors and bromide ion donors.

-13-

The proportion of hypochlorite donor and bromide ion donor in the composition or combination added to the system is selected to maintain an optimum ratio of all bromine containing species to the sum of all hypohalite species in the recirculating water. It has now been found that significant amounts of bromide ion are lost from recirculating water systems through the pathways of volatilization of hypobromous acid and bromamines and of formation of stable organobromine compounds. Moreover, hypochlorite species, hypobromite species, and bromide ion are lost from the recirculating water at different rates. These loss rates must be known in order to prescribe at what rates to feed the hypochlorite donor and bromide ion donor to the water to compensate for the losses and maintain the desired steady state concentrations.

It is very important, therefore, to control the chemistries of the reactions of the hypochlorite species with the bromide ion (equations 6a and 6b) in a dynamic system. More specifically, it is critical to control the mole ratio of the sum of all bromine-containing species (HOBr , OBr^- and Br^-) to the sum of all hypohalite species (HOBr , OBr^- , HOCl and OCl^-) present in the water. For the purposes of this discussion, this mole ratio will be referred to herein as the "chlorine-to-bromine conversion ratio" or "Conversion Ratio" ("CR") and will be written as:

$$\text{CR} = \frac{\text{moles of } (\text{HOBr} + \text{OBr}^- + \text{Br}^-)}{\text{moles of } (\text{HOBr} + \text{OBr}^- + \text{HOCl} + \text{OCl}^-)}$$

This ratio will be used hereafter because it is a convenient way to express the instantaneous measure of the extent of conversion of the hypochlorite species to hypobromite species. It is also a convenient way to establish if the hypochlorite donor/bromide ion donor

-14-

compositions are actually performing as a bromine biocide, a mixture of bromine and chlorine biocides, or as a chlorine biocide only. For example, consider the following four scenarios.

5

In the first scenario, the recirculating water does not contain any bromide ion. It follows then that there will be no hypobromite species present. Since the $[\text{Br}^-] = 0.0$ and the $[\text{HOBr}] = [\text{OBr}^-] = 0.0$, then hypochlorite
10 species will have some finite values; e.g., 0.5 mole of HOCl and 0.5 mole of OCl^- . Also, $\text{CR} = 0.0$ as shown by the following calculation:

$$\text{CR} = \frac{(0.0 + 0.0 + 0.0)}{(0.0 + 0.0 + 0.5 + 0.5)} = \frac{0.0}{1.0} = 0.0$$

15

Under these conditions, the biocide will perform as a chlorine biocide.

20 Assume in the second scenario that the recirculating water contains 0.5 mole of bromide ion, 0.5 mole of HOCl and 0.5 mole of OCl^- before the hypochlorite species/bromide ion reactions occur. Under these conditions, there is only enough bromide ion to satisfy
25 one-half of the stoichiometric requirements of the reactions outlined in equations 6a and 6b. Therefore, essentially all of the bromide ions will be converted to hypobromite species, but only one-half the hypochlorite species will be converted to hypobromite species. Also,
30 one-half the hypochlorite species will still be present. Thus, the hypohalite species in the water will be a 50/50 mixture of hypochlorite species and hypobromite species and the CR will be 0.5 as shown by the following calculation:

35

-15-

$$[\text{HOBr}] + [\text{OBr}^-] = 0.5 \text{ mole}$$

$$[\text{HOCl}] + [\text{OCl}^-] = 0.5 \text{ mole}$$

$$[\text{Br}^-] = 0.0$$

$$\text{CR} = \frac{(0.5 + 0.0)}{(0.5 + 0.5)} = \frac{0.5}{1.0} = 0.5$$

10 Since the hypochlorite donor/bromide ion donor composition is capable of only maintaining a 0.5 Conversion Ratio, it will exhibit biocidal properties intermediate between that of a chlorine biocide and a bromine biocide. It follows then that any hypochlorite
15 donor/bromide ion donor composition that maintains a Conversion Ratio between 0.0 and 1.0, will exhibit the same properties.

In the third scenario, assume that there are 1.0 mole
20 of bromide ion and 1.0 mole of hypochlorite species (0.5 mole of HOCl and 0.5 mole OCl⁻) before the HOCl/Br⁻ and OCl⁻/Br⁻ reactions occur. Under these circumstances, essentially all of the hypochlorite species will be converted to hypobromite species. Similarly, essentially
25 all of the bromide ions will be converted to hypobromite species. Hence, there will be essentially no hypochlorite species and bromide ions left. As a consequence, after the reactions, the Conversion Ratio will be 1.0 as shown by the following calculation:

30

$$[\text{Br}^-] = 0.0$$

-16-

$$[\text{HOCl}] = [\text{OCl}^-] = 0.0$$

$$[\text{HOBr}] + [\text{OBr}^-] = 1.0$$

5
$$\text{CR} = \frac{(1.0 + 0.0)}{(0.0 + 1.0)} = \frac{1.0}{1.0} = 1.0$$

And, the hypochlorite donor/bromide ion donor composition will perform as a bromide biocide.

10

Finally, in the fourth scenario, assume that the recirculating water contains 1.2 moles of bromide ion and 1.0 mole of hypochlorite species before the hypochlorite species react with the bromide ion. Upon completion of
15 these instantaneous reactions, the recirculating water will contain essentially no hypochlorite species, 1.0 mole of hypobromite species and 0.2 mole of bromide ion. Accordingly, after the reactions, the Conversion Ratio will be 1.2 as shown below:

20

$$[\text{HOCl}] = [\text{OCl}^-] = 0.0$$

$$[\text{HOBr}] + [\text{OBr}^-] = 1.0$$

25

$$[\text{Br}^-] = 0.2$$

Thus,

30
$$\text{CR} = \frac{(1.0 + 0.2)}{(1.0 + 0.0)} = \frac{1.2}{1.0} = 1.2$$

As a consequence, the hypochlorite donor/bromide ion donor composition will perform as a bromine biocide.

35

Thus, it is desirable to maintain the Conversion Ratio preferably at or slightly above 1.0. However, as

-17-

will be shown later, there are circumstances where other Conversion Ratios are desirable. Hence, it is preferable to maintain the Conversion Ratio between about 0.2 and 20.0 and most preferably between 0.5 and 4.0.

5

In order to control the Conversion Ratio to maintain a small excess of bromide ion, enough bromide ion must be fed to the water to compensate for any significant losses of bromine containing species. Bromide ion is, of course, lost from recirculating water systems through blowdown or turnover. These terms refer to water that is bled from the system, a practice necessary to keep dissolved solids from building up to the point where scaling occurs. However, there has been no recognition in the literature that bromide ion is lost by volatilization of hypobromous acid and bromamines when combinations of hypochlorite donors and bromide ion donors are used to generate hypobromite species. Moreover, the literature contains no recognition that significant bromide ion losses can occur through the reaction of hypobromite species with organic materials in the recirculating water. Nor has the literature recognized the magnitude and the rate of bromide ion losses that can result from the volatilization and organobromine compound pathways. More importantly, the literature contains no recognition that knowledge of the bromide ion loss phenomenon may be used to develop compositions comprising hypochlorite donors and bromide ion donors that are capable of simultaneously compensating for the bromide ion losses and satisfying the chlorine demand of the recirculating water. Without knowledge of bromide ion loss pathways, as will be shown in the detailed description of this invention, it is virtually impossible to develop commercial products that will perform like bromine-based biocides without using a large excess of bromide ion. Thus, all significant pathways of bromide ion loss must be accounted for in order to

-18-

maintain an optimum Conversion Ratio in the recirculating water.

The failure of the prior art to adequately compensate
5 for bromide ion loss is evident in the prior art's use of
either large excesses of bromide ion or of insufficient
amounts to maintain maximum biocidal activity. Any large
excess of bromide ion is wasted since it is eventually
discarded, for example, in the cooling tower blowdown or
10 pool water turnover. Also, as will be shown in the
detailed description of the present invention, a large
excess of bromide ion is unnecessary because the physical
and chemical dynamics of the recirculating water system
will force the bromide ion concentration to a steady state
15 condition. In many cases, this will result in
considerable loss of bromide ion. As a consequence, it is
preferable and more economical to supply only sufficient
bromide ion to the recirculating water to maintain the
Conversion Ratio at, or slightly above, 1.0 to ensure
20 maximum biocidal effectiveness.

In one aspect, the present invention provides a
biocide composition containing a hypochlorite donor and a
bromide ion donor in amounts sufficient to satisfy the
25 chlorine demand of the system and maintain an optimum
Conversion Ratio.

In another aspect, the present invention provides a
method of treating recirculating water which comprises the
30 steps of ascertaining the rates of bromide ion loss from
the system due to blowdown, volatilization, and formation
of stable organobromine compounds and adding a
hypochlorite donor and a bromide ion donor in amounts
sufficient to compensate for the bromide ion losses and
35 maintain an optimum Conversion Ratio.

-19-

Suitable hypochlorite donors include gaseous chlorine, alkali metal and alkaline earth metal hypochlorites, chlorinated hydantoins, chlorinated oxazolidinones, chlorinated imidazolidinones, and
5 chlorinated isocyanuric acid derivatives.

Suitable bromide ion donors include liquid bromine, bromine chloride, alkali metal and alkaline earth metal bromides, quaternary ammonium bromides, bromamines,
10 brominated hydantoins, brominated sulfonamides, brominated succinimides, brominated oxazolidinones, brominated imidazolidinones, brominated isocyanurates, and salts of trihalide or mixed trihalide ions containing bromine.

15 In a preferred embodiment the hypochlorite donor and bromide ion donor are dry solids having a higher dissolution rate and a higher water solubility than hydantoins. Preferred dry solids include trichloroisocyanuric acid or sodium or potassium
20 dichloroisocyanurate and sodium or potassium bromide. When these compounds are used, it has been found that proportions of about 85 to about 99 parts by weight hypochlorite donor and about 1 to about 15 parts by weight bromide ion donor are capable of maintaining the
25 Conversion Ratio in the optimum range for most water systems. In other instances, e.g. when hydantoin derivatives are used as the bromide ion donor, different proportions are sometimes necessary. For these compounds, it has been found that proportions of about 50 to about 99
30 parts by weight hypochlorite donor and about 1 to about 50 parts by weight bromide ion donor are capable of maintaining an optimum Conversion Ratio.

It has now also been found that certain compounds can
35 be added to the recirculating water system to suppress the loss of bromide ions through volatilization of hypobromous

-20-

acid and bromamine. The bromine volatilization suppressants may be included in the hypochlorite donor/bromide ion donor biocide composition or combination thereof or may be added separately to the recirculating water. Suitable bromine volatilization suppressants include hydantoin derivatives, sulfonamide derivatives, sulfamic acid derivatives, glycoluril derivatives, oxazolidinone derivatives, imidazolidinone derivatives and succinimide derivatives.

10

Other features and advantages of the present invention will become apparent from the following detailed description, which is given by way of illustration only.

15

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 illustrates the effect of the Conversion Ratio on killing efficiency.

20

FIGURES 2-6 illustrate the effect of the hypochlorite donor/bromide ion donor composition on the Conversion Ratio in the recirculating water and the ability of the biocide to perform as a bromine biocide. NaBr/ACL90 PLUS and NaBr/ACL60 compositions are used to illustrate the effects.

25

FIGURE 7 illustrates the effect of DMH on the Henry's Law constant for a bromine biocide.

30

DETAILED DESCRIPTION OF THE INVENTION

A hypochlorite donor compound according to the present invention may be any chlorine containing compound capable of providing a sufficient amount of hypochlorite species in aqueous solution, including but not limited to gaseous chlorine, hypochlorite salts such as lithium

35

-21-

hypochlorite, sodium hypochlorite, or calcium hypochlorite, chlorinated hydantoins such as dichlorodimethylhydantoin, or bromochlorodimethylhydantoin, chlorinated oxazolidinones such as 3-chloro-
5 4,4-dimethyl-2-oxazolidinone, chlorinated imidazolidinones such as 1,3-dichloro-4,4,5,5-tetramethyl-2-imidazolidinone, or chlorinated isocyanuric acid or its derivatives including its salts, hydrates, complexes, or mixtures thereof.

10

Some disadvantages may occur with the use of certain of these hypochlorite donor compounds. For example, addition of calcium is not desirable since repeated use could increase the calcium ion concentration in the water
15 to the level where calcium scaling problems could occur. Since chlorine gas is a hazardous material, its use is generally limited to the larger, more sophisticated recirculating water systems. Finally, many of the chlorinated organic compounds are less useful than the
20 chlorinated isocyanuric acid derivatives due to higher costs, lower dissolution rates, lower halogen content, and/or the buildup of species which inhibit biocidal activity.

25 Preferred hypochlorite donor compounds include chlorinated isocyanuric acid derivatives chosen from the following group of compounds: sodium dichloro-s-triazinetriene (also called sodium dichloroisocyanurate, available from Monsanto Co. under the tradename ACL60),
30 potassium dichloro-s-triazinetriene (available from Monsanto Co. under the tradename ACL59), the hydrate of sodium dichloro-s-triazinetriene (available from Monsanto Co. under the tradename ACL56), dichloroisocyanuric acid, trichloro-s-triazinetriene (also called
35 trichloroisocyanuric acid, available from Monsanto under the tradename ACL90 PLUS), mixtures thereof such as

-22-

[mono(trichloro)-tetra(monopotassium dichloro)]-penta-s-triazinetriene and [mono(trichloro)-mono(monopotassium dichloro)]-di-s-triazinetriene. These compounds are disclosed, for example, in U.S. Patents 3,035,056;
5 3,035,057; 3,150,132; 3,256,199; 3,294,797; and 3,564,146.

The bromide ion donor according to the present invention may be any compound capable of providing a sufficient amount of bromide ion in aqueous solution
10 including, but not limited to, liquid bromine, bromine chloride, alkali metal bromides, alkaline earth metal bromides, R_4 -ammonium bromide where R is an alkyl or aryl group, bromamines, N-brominated organic compounds, such as N-brominated hydantoins, N-brominated sulfonamides, N-
15 brominated oxazolidinones, N-brominated imidazolidinones, N-brominated imides such as N-bromosuccinimide or N-brominated isocyanurates which can release hypobromite species or salts of trihalide or mixed trihalide ions such as Br_3^- or $ClBr_2^-$ as described in U.S. Patent 3,152,073.

20

The hypochlorite donor compound and the bromide ion donor compound may be added either separately or as a single composition. For some combinations, the two components must be added separately, for example, chlorine
25 gas and sodium bromide. In many cases, however, it is advantageous to premix the two components and add the compositions to the recirculating water system. This reduces the number of materials to be handled and thus the number of controls required. Thus, it is possible to
30 introduce the biocide of the present invention into the recirculating water system by any of the following means: an erosion feeder, a floater, porous bags, perforated buckets or by hand dosing.

35 A preferred product is a solid dry mixture of a chlorinated isocyanuric acid derivative and a bromide ion

-23-

donor, most preferably compacted in the form of a tablet, stick or puck. One or more compacting aids such as boric acid, sodium stearate, potassium stearate, aluminum hydroxide or monoglycerol stearate may optionally be used.

5 To eliminate any possible interaction between the two components of the mixture it is necessary to eliminate any free water, as taught in U.S. Patent 2,815,311. If free water is present, the two components may react to form bromine gas, which can corrode metallic containers or pose

10 a health hazard to persons handling the material. In addition to optional compacting aids, the biocide of the present invention may also optionally include one or more scale inhibitor compounds such as polymaleic acid, polyacrylic acid, a phosphonate, a polyphosphate, or

15 mixtures thereof.

When the product used is a mixture of a solid hypochlorite donor and a bromide ion donor, the appropriate composition depends on the operating

20 characteristics of the individual recirculating water system. Therefore a range of compositions is required since there are a number of differences between systems. These differences include variation in the quality of the water used for makeup, variation in local air quality,

25 variation in the blowdown or turnover rate, and other system variables. For a composition of trichloroisocyanuric acid and sodium bromide, the weight percent of sodium bromide in the composition required to provide the optimum Conversion Ratio in the recirculating

30 water typically ranges from about 3% NaBr to about 15% NaBr, depending on how the recirculating water system is operated.

To maintain the Conversion Ratio in solution at the

35 desired optimum, it is necessary to control both the sum of the concentrations of the hypohalite species (HOCl ,

-24-

OCl^- , HOBr , and OBr^-) and the sum of the concentrations of all bromine containing species (HOBr , OBr^- , and Br^-).

Control of the free halogen concentration is straightforward and is normally achieved for most systems, either with automated analyzer/control equipment or manually with the use of analytical test kits. Test kits and analytical control equipment determine free halogen concentrations by measuring the oxidizing potential of the species dissolved in the water. However, these devices are incapable of distinguishing whether the oxidizing potential was due to hypochlorite or hypobromite species. Consequently, the free halogen concentrations measured in the recirculating water systems are the sum of the free chlorine and the free bromine, and will usually be expressed in terms of free chlorine, since chlorine test kits are more widely used. The free halogen concentrations may also be expressed in terms of free bromine by: (1) multiplying the free chlorine reading by 2.25, which is the ratio of the molecular weights of molecular bromine to molecular chlorine ($160/71 = 2.25$) or (2) using a bromine test kit. However, when the Conversion Ratio in the recirculating water is one or greater, all of the free halogen species will be present as free bromine species, even though the free bromine may be expressed in terms of free chlorine.

Initially, it was believed that bromide ion would be a conserved specie in recirculating water systems, that is, that blowdown or turnover would be the only significant pathway for bromide ion loss. Blowdown or turnover loss, $\text{BrL}(\text{BD})$, may be calculated using the following equation, assuming constant bromide ion concentration:

-25-

$$\text{BrL(BD)} = Q_b \times C_{\text{Br}} \times \frac{3.79}{1000} \quad (9)$$

where: BrL(BD) = bromide ion loss due to blowdown,
gm/day

Q_b = blowdown or turnover rate, gal/day

C_{Br} = total concentration of all bromine
species, mg/liter

3.79 = conversion factor, gallons to
liters

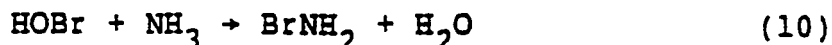
1000 = conversion factor, grams to
milligrams

Example: a system contains 1.0 mg Br/liter distributed
between bromide ion and hypobromite species, and has a
blowdown rate of 1000 gal/day. The calculated bromide ion
loss due to blowdown would then be 3.79 gm Br/day.

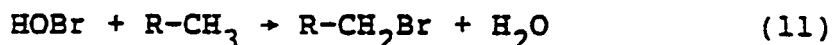
Measurement of the bromide ion concentration during
initial experiments has unexpectedly revealed the
existence of other significant pathways of bromide ion
loss. Further investigation has now demonstrated that in
order to maintain an optimum Conversion Ratio, it is
necessary to compensate for bromide ion losses by three
additional pathways: 1) volatilization of hypobromous
acid, 2) volatilization of bromamines and 3) formation of
organobromine compounds. Loss of bromide ion by the
volatilization of hypobromous acid occurs as a result of
the reaction described in equation (6a).

Bromide ion losses via volatilization of bromamines
occurs as a consequence of the reaction between
hypobromous acid and nitrogenous contaminants (expressed
in terms of ammonia).

-26-



Organobromine compound formation occurs due to the reaction of hypobromous acid with organic matter in the water to form compounds with carbon-bromine bonds, for example:



10 The organobromine compounds include the trihalomethanes or other brominated alkanes, brominated carboxylic acids, and the like. The carbon-bromine bonds are very stable and not readily hydrolyzed. Hence, the bromine specie is no longer available as bromide ion for regeneration to
15 hypobromous acid by hypochlorous acid. Therefore, the bromide ion has been effectively removed from this chemical recycle loop.

It is necessary to establish the magnitude of the
20 bromide ion losses by these pathways in order to determine the appropriate proportions of bromide ion donor and hypochlorite donor to feed to the recirculating water system. This can be accomplished by two methods: 1) analytical determination of the decrease in bromide ion
25 concentration ("the bromide ion analytical method") and 2) calculation of losses by the different pathways.

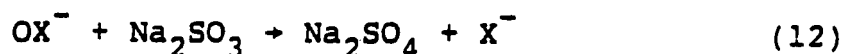
The determination of the appropriate amounts of bromide ion donor and hypochlorite donor can be achieved
30 by the bromide ion analytical method as outlined in the following:

1. Take samples of the recirculating water at regular intervals and note the sample times.

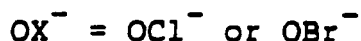
-27-

2. Determine the bromide ion concentration of the water samples with ASTM D-1246-82a, Method D - Ion Selective Electrode For Bromide. Note, in this case, the hypohalite species (HOBr , OBr^- , HOCl , OCl^-) must be converted to halide species (Cl^- and Br^-) prior to the determination of bromide ion. This is achieved by adding sodium sulfite to the solutions in amounts of 1.25 times the stoichiometric amount required to satisfy the following equation:

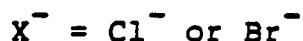
10



where:



15



3. Calculate the total daily loss of bromide ion TBrL , in grams per day by using the analytical and sample time data.

20

4. Determine the amount of bromide ion donor, BrD , required to compensate for the losses and maintain the bromide ion concentration at the desired level with the following equation:

25

$$\text{BrD} = \frac{M_{\text{BrD}}}{M_{\text{Br}}} \times \text{TBrL} \quad (13)$$

- 30 where: BrD = amount of bromide ion donor required to compensate for losses and maintain the bromide ion concentration at the desired level, gm/day

-28-

M_{BrD} = mole weight of bromide ion donor, gm

M_{Br} = mole weight of bromide ion, gm

5 $TBrL$ = total daily bromide ion losses, gm/day

5. Determine the daily chlorine demand, CD, of the system.

10 6. Determine the amount of hypochlorite donor compound required to satisfy the daily chlorine demand with the following equation:

15
$$HCD = \frac{CD}{AvC} \times 100\% \quad (14)$$

where: HCD = amount of hypochlorite donor compound required to satisfy the chlorine demand, gm/day

20 CD = chlorine demand of the system, gm Cl_2 /day

AvC = available chlorine content of chlorine donor (wt %)

25 7. For hypochlorite donor/bromide ion donor combinations where it is more practical to feed the two donors separately, the results of steps 4 and 6 indicate what the feed rates must be for the corresponding donors
30 in order to satisfy the chlorine demand and bromide ion donor requirements and to make the combinations perform as bromine biocides.

 8. For a hypochlorite donor/bromide ion donor
35 combination that will be contained in a single composition or product, a composition is determined by the following calculations:

-29-

a. Hypochlorite Donor/Bromide Ion Donor
Composition Requirements

$$\text{BGC} = \text{HCD} + \text{BrD} \quad (15)$$

5

where: BGC = amount of hypochlorite donor/bromide ion donor composition required to satisfy the chlorine demand and bromide ion requirements simultaneously, gm/day

10

b. Hypochlorite Donor/Bromide Ion
Donor Composition.

(16)

15

$$\% \text{ hypochlorite donor} = \frac{\text{HCD}}{\text{BGC}} \times 100\%$$

(17)

20

$$\% \text{ bromide ion donor} = \frac{\text{BrD}}{\text{BGC}} \times 100\%$$

Although it is an alternative to calculating the appropriate amounts of bromide ion donor and hypochlorite donor to feed to the system, the bromide ion analytical approach is generally beyond the sophistication of most cooling tower, swimming pool and spa operations or would require a considerable expense for added instrumentation.

The present invention obviates the need for this costly instrumentation, since the appropriate amounts of hypochlorite donor and bromide ion donor may also be established by the second method, that is, by calculating bromide ion losses. Investigations relating to the present invention demonstrate that the bromide ion can be lost by pathways other than blowdown. At the optimum Conversion Ratio, the losses incurred by these pathways can be several times larger than the blowdown loss, making it virtually impossible to maintain the desired Conversion

-30-

Ratio without knowledge of these pathways. The magnitudes of the losses by the various pathways are totally surprising. At Conversion Ratios much higher than optimum, the percentage of the total bromide ion lost by these pathways is much lower, because the ionic bromide form is not volatile. In such cases, the volatilization losses are not readily apparent. Thus, since prior art use of bromide-based biocides was not at the optimum Conversion Ratio, the loss of bromide ion by these pathways was not recognized. Because bromide ion was usually present in excess, the prior art did not perceive the importance of these additional bromide ion loss pathways.

The amount of bromide ion lost by flashoff of HOBr, BrL(FL), may be calculated using either equation (18) or (19).

$$\text{BrL(FL)} = \frac{f \times H_k}{W_L/W_G} \times R \times C_{\text{HOBr}} \times \frac{M_W}{M_a} \times \frac{M_{\text{Br}}}{M_{\text{HOBr}}} \times \frac{3.79}{1000} \quad (18)$$

or

$$\text{BrL(FL)} = f H_k Q_a D_a C_{\text{HOBr}} \times \frac{M_W}{M_a} \times \frac{M_{\text{Br}}}{M_{\text{HOBr}}} \times \frac{28.316}{1000} \times 1440 \quad (19)$$

where: BrL(FL) = amount of bromide ion lost by flashoff of hypobromous acid, gm Br/day

R = the recirculation rate of the recirculating water system, gal/day

35

-31-

f = flashoff equilibrium coefficient for the recirculating water system.
(Note, f has a value between 0 and 1.)

5 H_k = Henry's Law Constant for hypobromous acid at the pH and temperature of the recirculating water system

10 Q_a = the flow rate of air through the tower, ft^3/min .

D_a = density of air, gm/L

15 W_L/W_G = ratio of the mass flow rate of the recirculating water to the mass flow rate of air through the system

M_{HOBr} = mole weight of hypobromous acid, gm

20 C_{HOBr} = the concentration of hypobromite species as hypobromous acid, mg HOBr/L

M_W = mole weight of water, gm

25 M_a = mole weight of air, gm

M_{Br} = mole weight of bromide ion, gm

3.79 = conversion factor, gallons to liters

30 1000 = conversion factor, grams to milligrams

-32-

28.316 = conversion factor, cubic feet to
liters

1440 = conversion factor, days to minutes

5

It is important to point out that the value of C_{HOBr} , the concentration of hypobromite species, is not the same as C_{Br} , the sum of concentrations of all bromine-containing species, since some of the bromine species
10 present can be in the form of bromide ion.

Henry's Law constant is defined by the following equation:

15
$$H_k = \frac{C_{\text{solute (gas)}}}{C_{\text{solute (liquid)}}} \quad (20)$$

20 where:

 H_k = Henry's Law Constant $C_{\text{solute (gas)}}$ = concentration of volatile solute
in the gas phase

25

 $C_{\text{solute (liquid)}}$ = concentration of volatile solute
in the liquid phase

Henry's Law constant is, therefore, the ratio of the
30 concentration of solute in the vapor phase at equilibrium to the concentration of the solute dissolved in a solvent, in these cases water. This constant is a measure of the tendency of the dissolved solute to escape or volatilize from the solvent. A low Henry's Law constant indicates
35 little tendency for the solute to volatilize. A high constant value indicates a greater tendency of the solute to escape from the solution into the gas phase. Henry's Law constants can be expressed in any combination of a number of concentration units, such as partial pressure,

-33-

milligrams per liter, or mole fraction. Herein, mole fraction units are used for both the gas and liquid phase concentrations.

- 5 As an example, a cooling tower has $W_L/W_G = 1.3$, $f = 0.5$, $R = 400,000$ gallons/day, and the tower operates at pH = 8.0 and 30°C. For the conditions in this particular example, Henry's Law constant is 0.25. The concentration of free halogen is 0.5 mg/L (0.5 ppm, free chlorine
- 10 basis). The bromide ion concentration is maintained at 0.8 mg/L (0.8 ppm) to give a Conversion Ratio of 1.05, slightly greater than the optimum value of 1. Thus, all of the free halogen species are essentially free bromine species (HOBr and OBr^-). As a result, the free bromine
- 15 concentration in terms of hypobromous acid is 0.685 mg/L. $[C_{HOBr} = FAVC \times M_{HOBr}/M_{Cl_2} = 0.5 \times 96.9/71 = 0.685]$. Under these conditions, the flashoff loss of bromide ion via the volatilization of hypobromous acid is 51.1 grams of bromide ion per day. This loss is considerably larger
- 20 than that due to blowdown (cf. blowdown loss calculation above), demonstrating that volatilization of hypobromous acid can be a major factor contributing to the loss of bromide ion from recirculating water systems.
- 25 The Henry's Law constant for hypobromous acid used in the above example was determined as follows, using a pilot scale cooling tower since there is no literature data for hypobromous acid or any of the bromamines. The pilot
- 30 cooling tower was a counterflow type with a capacity of 80 liters of water, which was circulated through the tower at 1.2 gal/min. The air flow rate was 2800 L/min. An electrical heater, placed in the recirculation line, provided a constant heat source. In each experiment, the pilot tower was filled with chlorine-demand-free water and
- 35 an appropriate amount of biocide was added to give 4.0 mg/L (as chlorine). During the test, the biocide

-34-

concentration was continuously monitored using a Hach CL17 chlorine analyzer. The water was initially recirculated with no air flow for 30 minutes to establish a baseline free halogen concentration. The air flow was then started
5 and the free halogen concentration was monitored for four hours. The drop in the halogen concentration during this period, which is due to volatilization of any volatile species, can be used to calculate the Henry's Law constant using the following equation:

10

$$H_k = - \frac{(\log C_f - \log C_i)}{t} \times \frac{2.303 V_w D_w M_a}{Q_a D_a M_w}$$

15

where: H_k = Henry's Law constant at temperature and pH of the experiment

20

V_w = volume of recirculating water, liters

D_w = density of water, gm/ml

D_a = density of air, gm/ml

25

M_w = mole weight of water, gm

M_a = mole weight of air, gm

Q_a = volumetric air flow, L/min

30

C_f = final halogen concentration, mg/L

-35-

 C_i = initial halogen concentration, mg/L t = length of time of experiment, min

5

This procedure assumes that the hypobromous acid has reached equilibrium between the gas and liquid phases. With this method, Henry's Law constants were determined for hypobromous acid as a function of pH, temperature, and the concentration of additional chemical species.

As stated previously, the presence of ammonia in the recirculating water has also been found to increase the loss of bromide ion. This is due to the formation of various bromamine compounds, especially monobromamine, which is more volatile than hypobromous acid. The effect of ammonia on the volatility of hypobromous acid is reflected in an increase in the Henry's Law constant. This change in the Henry's Law constant is dependent on the ratio of ammonia to free bromine, the pH, and the temperature. There are no literature values for the Henry's Law constants for bromamines. The results of our measurements indicate the Henry's Law constant for bromamines is considerably larger than the Henry's Law constant for hypobromous acid under the same conditions. The simple bromamines are, therefore, very volatile and do not build up to significant levels because they are flashed off very rapidly.

Under steady state conditions, the loss of the simple bromamines by flashoff will be approximately equal to the rate of formation of monobromamine. The bromamine formation rate is determined by the rate of introduction of ammonia into the recirculating water. In most cases, the major source of ammonia is the makeup water. Thus,

-36-

the flashoff loss due to formation of bromamines, BrL(BA), can simply be estimated by the following equation:

$$\text{BrL(BA)} = C_{\text{NH}_3} \times Q_m \times \frac{M_{\text{Br}}}{M_{\text{NH}_3}} \times \frac{3.79}{1000} \quad (21)$$

where: BrL(BA) = amount of bromide ion lost by flashoff of bromamines, gm/day

10

C_{NH_3} = concentration of ammonia in makeup water, mg/L

15

Q_m = makeup water rate, gal/day

M_{Br} = mole weight of bromide ion, gm

M_{NH_3} = mole weight of ammonia, gm

20

3.79 = conversion factor, gallons to liters

1000 = conversion factor, grams to milligrams

25

Note, equation (21) applies only to relatively small ammonia concentrations.

Another significant pathway for bromide ion loss is the formation of organobromine compounds as a result of the reaction of hypobromous acid with organic molecules dissolved or suspended in the water. Carbon-bromine covalent bonds are usually stable to hydrolysis so that the bromine is not released back into the water and is not available for regeneration to hypobromite species. The amount of bromide ion loss can vary widely depending on the organic content of the water, which can be quantified

-37-

as TOC. TOC, or total organic carbon (in mg/L), measures the total amount of organic material dissolved or suspended in the water, without distinguishing the chemical form. Several commercial analyzers are available which perform this analysis. Lab experiments with both tap water and untreated surface water have shown that about 0.2 mg/L of bromide ion is combined as organobromine compounds for every mg/L of TOC introduced into the water. This number varies somewhat depending on the individual water source, but 0.2 is a reasonable estimate for most cases.

The amount of bromide ion loss caused by the formation of organobromine compounds, BrL(OBr) can be calculated with the following equation, which accounts for the total organic carbon introduced with the makeup water:

$$\text{BrL(OBr)} = Q_m \times 0.2 \times \text{TOC} \times \frac{3.79}{1000} \quad (22)$$

where: BrL(OBr) = amount of bromide ion lost due to the formation of organobromine compounds, gm/day

Q_m = makeup water rate, gal/day

TOC = total organic content of makeup water, mg/L

0.2 = amount of bromide ion lost per mg/L of TOC in recirculating water, mg/L

-38-

3.79 = conversion factor, gallons to
liters

1000 = conversion factor, grams to
milligrams

5

Note, equation (22) applies only to relatively small TOC concentrations. This calculation does not account for any TOC added from sources other than makeup, for instance, organic or biological contamination absorbed from the air blown through the tower or contamination from process leaks. If such contamination is severe, the additional loss of bromide ion by reaction with these sources of TOC should also be accounted for.

15

It is necessary to quantify the major pathways of bromide ion loss, blowdown, flashoff, and organobromine formation in order to determine the appropriate proportions of bromide ion donor and hypochlorite donor to feed to the recirculating water system. Once each of the bromide ion pathway losses are quantified, the optimum proportions of bromide ion donor and hypochlorite donor to be fed to the system may be calculated according to the following steps:

25

1) Define the desired-free halogen concentration (available chlorine basis), FAVC, and the desired Conversion Ratio, CR. CR may range from about 0.2 to about 20.0, more preferably from about 0.2 to about 10.0, and most preferably from about 0.5 to about 4.0. If excess bromide ion is desired CR should be greater than 1.0; if not, then CR can be less than 1.0.

2) Convert the desired free halogen concentration
35 to the concentration of hypobromous acid, C_{HOBr} , by
multiplying the free chlorine concentration, $FAvC$, by 1.37

-39-

x CR if CR is less than 1.0 or by 1.37 if CR is greater than 1.0. The factor 1.37 is equal to $96.916/70.906$ (molecular weight of HOBr/molecular weight of chlorine).

- 5 3) Calculate the desired total concentration of all
bromine containing species, C_{Br} , in terms of bromide ion,
using the following equation:

$$C_{Br} = FAVC \times CR \times \frac{M_{Br}}{M_{Cl_2}}$$

- 4) Calculate the daily bromide ion loss caused by blowdown, $BrL(BD)$, with equation (9).

- 5) Calculate the daily bromide ion loss incurred by the flashoff of hypobromous acid, BrL(FL) , using either equation (18) or (19).

- 20 6) Calculate the daily bromide ion loss caused by
bromamine flashoff, $\text{BrL}(\text{BA})$, with equation (21).

- 7) Calculate the daily bromide ion loss caused by the formation of organobromine compounds, $\text{BrL}(\text{OBr})$, using equation (22).

- 8) Calculate the total daily bromide ion loss, TBrL, by combining the results of the calculations in steps 4, 5, 6, and 7.

-40-

$$TBrL = BrL(BD) + BrL(FL) + BrL(BA) + BrL(OBr) \quad (23)$$

9) Determine the daily quantity of bromide ion donor required to compensate for bromide ion losses with equation (13).

10) Determine the amount of hypochlorite donor required to satisfy the daily chlorine demand with equation (14).

10

11) For hypochlorite donor/bromide ion donor combinations where it is more practical to feed the two donors separately, the results of steps 9 and 10 indicate what the feed rates must be for the corresponding donors in order to satisfy the chlorine demand and bromide donor requirements simultaneously and make the combination perform as a bromine biocide.

12) For products containing both the hypochlorite donor and bromide ion donor as a single composition or mixture, determine the appropriate composition with equations (15), (16) and (17).

The effectiveness of the hypochlorite donor/bromide ion donor biocides and the bromine volatilization suppressants disclosed herein is demonstrated in the following examples, including killing efficiency experiments, cooling tower and spa tests, and calculations in which compositions representative of the present invention, such as ACL60/NaBr and ACL90 PLUS/NaBr, are compared with chlorine (ACL60) and competitive bromine (BCDMH) biocides.

-41-

Example 1 - Effectiveness of Hypochlorite Donor/Bromide
Ion Donor Compositions In Cooling Towers

5 A small crossflow, induced draft cooling tower, used
to cool a 250 ton air conditioning system, was used to
test the relative effectiveness of the current invention
versus chlorine and BCDMH biocides over a period of five
months. The pH of the tower water was controlled at 8.5
10 and the free halogen concentration was controlled at 0.5
mg/L (available chlorine base) with an automated chlorine
analyzer/controller. Scale and corrosion inhibitors were
also added as part of the normal operation of the cooling
tower. The effectiveness of each biocide was judged on
15 the ability of the biocide to control the biofouling
microorganism population as measured by a standard plate
count method. Microorganism populations were reported as
colony forming units per milliliter (CFU/ml). Samples for
the determination of microorganism populations and bromide
20 ion concentration were taken from the same location in the
cooling tower basin away from the point of chemical
addition. Two to three samples were taken per day.
Immediately after sampling, any hypohalite species were
reduced to halide species with sodium thiosulfate. The
25 bromide ion concentration was measured by ion
chromatography. The results of the test are shown below
in Table 1:

-42-

TABLE 1

Results of Cooling Tower Biofouling Control Tests
 Comparing Biocidal Effectiveness of Hypochlorite
 5 Donor/Bromide Ion Donor Biocide Compositions to Chlorine
 and Bromine Biocides.

10	Biocide Tested -----	Total Br Conc (mg/L) -----	Plate Count (CFU/ml) -----	Conversion Ratio -----
	ACL60	0.0	14,200	0.0
15	ACL60/NaBr	0.14	5,600	0.25
	ACL90 PLUS/NaBr	1.8	4,200	3.2
	BCDMH	23.2	24,600	41.1
20	ACL60/NaBr	18.	1,600	31.9
	ACL90 PLUS/NaBr	6.5	1,200	11.5

25 Notes:

1. Results are the average values observed during the
 test periods. 2. Test Conditions: pH = 8.5; free
 halogen = 0.5 mg/L, available chlorine basis.

30

In these tests, ACL60 (sodium dichloroisocyanurate)
 was used to demonstrate the biocidal effectiveness of
 chlorine biocides under these conditions. Combinations of
 sodium bromide with ACL60 and sodium bromide with ACL90
 35 PLUS (trichloroisocyanurate) were employed to illustrate
 the effect of the Conversion Ratio on the biocidal
 effectiveness of the hypochlorite donor/bromide ion donor
 compositions, which are representative of the present
 invention, and their ability to perform as bromine
 40 biocides. BCDMH was also included to compare the
 effectiveness of this bromine biocide to the ones
 representative of the present invention.

-43-

The results of these tests show that the hypochlorite donor/bromide ion donor compositions of NaBr/ACL60 and ACL90 PLUS/NaBr, were not only superior to the chlorine biocide, ACL60, but were also superior to the bromine
5 biocide, BCDMH, in controlling the population of the biofouling microorganisms. The most effective NaBr/ACL60 and NaBr/ACL90 PLUS biocide compositions were those which maintained the Conversion Ratio in the recirculating water above 1.

10

The biocide compositions that were less effective were those which produced Conversion Ratios of less than one. However, all of the NaBr/ACL compositions were more effective than the chlorine (ACL60) and BCDMH biocides, as
15 evidenced by the fact that they controlled the biofouling microorganism population at or below 6000 CFU/ml, whereas the chlorine and BCDMH biocides were not capable of reducing the biofouling populations below 14,000 and 24,000 CFU/ml, respectively, at the same free halogen
20 concentration.

Example 2 - Effectiveness of Hypochlorite Donor/Bromide Ion Donor Biocide Compositions in Biofouling Control
25 Experiments.

The killing efficiencies of the biocides evaluated in Example 1 were also determined in laboratory experiments designed to simulate cooling tower conditions. In these
30 experiments, a culture of microorganisms from the cooling water in Example 1 were cultured in a well-stirred vessel by metering nutrient solution into the solution containing the culture. The vessel contents were maintained at 37°C and pH of 8.0. Each experiment consisted of shocking the
35 microorganisms with the biocide to be tested. Nutrient solution was also fed continuously to the vessel to

-44-

encourage growth of the microorganisms and biocide solution was fed to the vessel to control the free halogen concentration at 0.5 mg/L (available chlorine basis) and the microorganism population. The microorganism
5 population was determined periodically by an HMB-II apparatus (KVM Engineering) until the microorganism population had ceased to decline and remained constant for several hours. This usually occurred in about four hours after the start of the experiment. At this point, the
10 microorganism growth rate and the microorganism death rate due to the biocidal activity of the biocide were considered to be in dynamic equilibrium, or at steady state. The effectiveness of biocide was then judged on the basis of killing efficiency as defined by the
15 following expression.

$$KE = \frac{[P_i - P_f]}{P_i} \times 100\% \quad (24)$$

20 where: KE = killing efficiency of the biocide, %

P_i = microorganism population at the start of the experiment, CFU/ml

25 P_f = microorganism population at steady state conditions, CFU/ml

The results of the biocide killing efficiency experiments are summarized in Table 2.

-45-

TABLE 2

Results of Biocide Killing Efficiency Experiments

	Biocide Tested	NaBr/ACL 60 Wt. Ratio	CR	P _i (CFU/ml)	P _f (CFU/ml)	KE
	BCDMH	-.-	-.-	2,140,000	1,260,000	41
10	ACL60	0.0	0.0	1,560,000	880,000	44
	ACL60/NaBr	0.1	0.13	1,960,000	830,000	58
15	ACL60/NaBr	0.19	0.22	1,410,000	350,000	75
	ACL60/NaBr	1.0	1.20	1,460,000	165,000	89

20 Conditions: pH = 8.5, temperature = 37° C, free
halogen = 0.5 mg/L (available chlorine basis).

25 The results in Table 2 show that the NaBr/ACL60
compositions (hypobromous acid generating compositions)
have superior biocidal activity relative to the chlorine
biocide, ACL60, and the bromine biocide, BCDMH, under the
conditions of the experiments. The results also support
the validity of the results obtained in the cooling tower
tests (Example 1). The above results also show that the
30 best killing efficiency was obtained at a Conversion Ratio
of 1.20. This represents the condition where the amount
of NaBr is sufficient to make the bromide ion
concentration in the water slightly in excess of the
stoichiometric amount required to satisfy the reactions
35 shown in equations (6a) and (6b). Thus, the best killing
efficiency was obtained with the composition that
performed as a true bromine biocide. However, the results
of the experiments indicate that the killing efficiencies
of NaBr/ACL60 compositions which yield Conversion Ratios
40 of less than 1 are still better than the chlorine (ACL60)
or BCDMH biocides.

-46-

The effect of the Conversion Ratio can be understood more clearly by referring to the graph shown in Figure 1. Figure 1 is a plot of the killing efficiency of each ACL60/NaBr composition tested as a function of the Conversion Ratio. The results show that killing efficiencies increase as the Conversion Ratios increase until the maximum killing efficiency is attained near a Conversion Ratio of 1.0. At this point, all of the free halogen species are free bromine species. Figure 1 also shows that most of the improvement in killing efficiency (from 42% to 75%) occurred between Conversion Ratios of 0.0 and 0.2. This indicates that the Conversion Ratio in the recirculating water system does not have to be controlled tightly in order for the bromine based biocide to be significantly better than chlorine biocides at pH levels of 8 or higher.

Even though the performance of the hypochlorite donor/bromide ion donor biocide will be very good at these low ratios, it is desirable to use these biocides at Conversion Ratios of 1.0 or more, because the biocides will control the microorganisms more effectively, thereby reducing biocide usage, and because the formation of chloramines will be minimized. Figure 1 shows at what levels the Conversion Ratio should be maintained to obtain maximum biocidal activity. However, it would not be economical, in most instances, to use products with proportions of bromide ion donor and hypochlorite donor equivalent to the desired Conversion Ratio in the recirculating water. Therefore, it is important to understand how to develop compositions and methods that allow hypochlorite donor/bromide ion donor compositions with low bromide ion donor contents to maintain the desired Conversion Ratio in the recirculating water.

-47-

Example 3 - Discovery of Bromide Ion Loss Phenomenon

During tests run on the cooling tower system described in Example 1, ACL90 PLUS (trichloroisocyanurate) was fed to the recirculating water system at a rate sufficient to maintain a free halogen concentration of 0.5 mg/L (0.5 ppm, free chlorine basis). The chlorine demand of the recirculating water system was determined to be about 282 grams of available chlorine per day. Since ACL90 PLUS, which has an available chlorine content of 90.7%, was used as the hypochlorite donor, the ACL90 PLUS requirement was 310.4 grams/day $[(282 \div 0.907) \times 100\%]$. Sodium bromide was fed to the system at a rate of 2.6 gm NaBr/day, a rate calculated to account for blowdown loss and maintain a bromide ion concentration of 0.56 mg/L, a concentration sufficient to maintain a Conversion Ratio of one. Analyses of water samples taken from the system revealed, however, that the bromide ion was consistently as low as about 0.05 mg/L, considerably below the desired bromide ion concentration of 0.56 mg/L. Therefore, the bromide ion was lost at a rate much higher than expected.

Example 4 - Demonstration of the Bromide Ion Loss Phenomenon

25

Tests were conducted in the following manner. The blowdown value for the recirculating water system of the cooling tower cited in Example 1 was closed to prevent the loss of water by this pathway. The recirculating water system was then dosed with enough sodium bromide to obtain a concentration of about 0.5 mg/L (0.5 ppm) of bromide ion. The free halogen was maintained at 0.5 mg/L (0.5 ppm, free chlorine basis). The water was then recirculated for about one hour to obtain a uniform concentration of bromide ion throughout the system. Water samples were then taken periodically over a 24 hour period

-48-

and analyzed for bromide ion. The results of the analyses in Table 3 show that about 70% of the bromide ions were lost during this 24 hour period. Loss rates for the first few hours were actually even higher. For instance, the
5 loss rate for the first 8.5 hours is over 6% per hour or 152% per day.

TABLE 3

10 Bromide Loss Data for Zero Blowdown

Water Sample -----	Time (hr) -----	Bromide Ion Conc (ppm) -----	Bromide Ion Losses (%) -----	Lithium Conc (ppm) -----
15				
1	0.0	0.50	0.0	0.42
2	8.5	0.20	54.0	0.40
3	24.0	0.13	69.0	0.41

20 To prove that the bromide ion losses were not due to leaks in the recirculating water system, the water was also spiked with lithium chloride at the start of this test. Lithium is not commonly found in water, can be easily analyzed for, and is not volatilized from the water
25 system. The water samples taken for bromide analyses were also analyzed for lithium. The results shown in Table 3 demonstrate that lithium was not lost from the system during the test, thereby demonstrating that the bromide ion losses were not due to leaks, but, instead were due to
30 other phenomena.

This example also demonstrates that the bromide ion losses can be significant in recirculating water systems, a fact not recognized by the prior art. In addition, it
35 shows that many of the compositions described in the prior art for mixtures of hypochlorite donors and bromide ion donors actually performed as chlorine biocides instead of performing as bromine biocides like the claimed compositions. Furthermore, the results clearly indicate
40 that without the knowledge of these losses, it would be

-49-

impossible to make hypochlorite donor/bromide ion donor compositions which would perform efficiently and economically as bromine biocides.

5 Example 5 - Compensation for Bromide Ion Loss

This example demonstrates that with knowledge of the existence of the bromide ion loss phenomena, bromide ion losses can be adequately compensated for to produce the
10 desired results -- performance of hypochlorite donor/bromide ion donor composition as bromine biocides. As shown in Example 3, prior to the discovery of the bromide ion loss phenomena, the sodium bromide was fed to the cooling water system at the rate of 2.6 grams/day, an
15 amount only sufficient to maintain a Conversion Ratio of 0.1 (0.05 ppm divided by 0.5 ppm free chlorine), far below the ratio required to make the free halogen species perform as a bromine biocide.

20 The results in Examples 3 and 4 indicated that the estimated sodium bromide feed rate had to be considerably higher than the original rate (2.6 grams/day) in order to maintain a Conversion Ratio of approximately one. Tests showed that a sodium bromide feed rate of 15-17 grams/day
25 maintained the desired bromide ion concentration. Furthermore, the biocidal system performed as bromine biocide as evidenced by the reduction in biofouling organism population from 14,000 CFU/ml for the 0.01 Conversion Ratio in Example 3 to 5000 CFU/ml.

30

-50-

Example 6 - Determination of Appropriate Hypochlorite Donor/Bromide Ion Donor Biocide Composition by the Bromide Ion Analytical Method.

5 The following is an example of how this method can be applied to the determination of the appropriate hypochlorite donor compound/bromide ion donor composition for this cooling tower system.

10 In Example 5, the bromide ion donor (sodium bromide) requirement was determined to be 15.0-17.0 gm/day in order to maintain the bromide ion concentration at the level necessary to make the biocide perform as a bromine biocide. The hypochlorite donor/bromine ion donor
15 composition requirement, BGC, for this particular combination was 327.4 grams/day (310.4 + 17.0). Therefore, the appropriate composition was 94.8% ACL90 PLUS $[(310.4 \div 327.4) \times 100\%]$ and 5.2% $[(17.0 \div 327.4) \times 100\%]$ sodium bromide.

20

 If it is desired to add these two donors as a single product, the ACL90 PLUS and sodium bromide may be blended together, compacted into tablets, placed in an appropriate erosion feeder, and used to satisfy the chlorine demand
25 and bromide ion requirements of the system. The composition would perform in the above described system as a bromine biocide. If it is desired to add the ACL90 PLUS and sodium bromide separately, the feed rates would be 310.4 and 17.0 gm/day respectively.

30

-51-

**Example 7 - Bromide Ion Loss and Composition Calculations
for Cooling Towers.**

An example of the procedure outlined above for
5 calculating the total bromide ion loss and the
hypochlorite donor/bromide ion donor composition required
to maintain the optimum Conversion Ratio is given below.
Three cooling towers, having the characteristics given in
Table 4A, will be used. The three towers are various
10 sizes and have somewhat different operating
characteristics. A major difference between the three
towers is the quality of the makeup water, which has a
significant impact on the amount of bromide ion loss.

-52-

TABLE 4A

Characteristics of Model Cooling Towers

5	Characteristic	Tower A	Tower B	Tower C
	Blowdown Rate, Q_b (gal/day)	1,000	2,000	12,000
10	Recirculation Rate, R (gal/day)	200,000	600,000	1.5×10^7
	Makeup Rate, Q_m (gal/day)	5,000	10,000	63,000
15	Desired Free Halogen Conc., FAVC (mg/L, as chlorine)	0.3	0.2	0.1
	Desired Conversion Ratio, CR	1.1	0.9	1.2
20	Flashoff Equilibrium Coefficient, f	0.5	0.5	0.5
	W_L/W_G	1.3	1.3	3.0
	Tower-Top Temperature ($^{\circ}\text{C}$)	30	30	30
25	pH	8.0	8.0	8.0
	Ammonia Concentration in Makeup Water (mg NH_3/L)	0.0	0.1	0.1
30	TOC Concentration in Makeup Water (mg TOC/L)	2.0	1.0	1.0
	Biocide Usage (grams ACL90 PLUS/day)	400	700	3,300

35 From the characteristics in Table 4A, the following
 parameters can be found for the three example towers.
 Sodium bromide (mol.wt. = 102.90 gm/mole) is used as the
 bromide ion donor and ACL90 PLUS is the hypochlorite
 40 donor.

-53-

TABLE 1B

Calculated Parameters of Model Cooling Towers

5	Calculated Parameter -----	Tower A -----	Tower B -----	Tower C -----
	HOBr Concentration, C_{HOBr} (mg/L)	0.410	0.246	0.137
10	Total Br Conc, C_{Br} (mg/L)	0.372	0.203	0.135
	Henry's Law Constant, H_k	0.250	0.250	0.250
15	Blowdown Loss, BrL(BD), grams Br/day	1.41	1.54	6.15
	HOBr Flashoff Loss, BrL(FL), grams Br/day	15.30	27.54	165.75
20	Bromamine Flashoff Loss, BrL(BA), grams Br/day	0.0	17.78	112.01
25	Organobromine Compound Formation Loss, BrL(OBr), grams Br/day	7.58	7.58	47.75
	Total Bromide Ion Loss, TBrL, grams Br/day	24.29	54.44	331.67
30	Total NaBr Needed, grams/day	31.28	70.10	427.09
	% NaBr Needed in ACL90 PLUS/ NaBr Composition	7.25	9.10	11.46

35

The above calculations show that the flashoff losses can be much larger than the blowdown loss, especially when ammonia is present. Given the values above, the appropriate composition of a trichloroisocyanuric acid/NaBr mixture is calculated to be 7.25% NaBr for Tower A, 9.10% NaBr for Tower B and 11.46% NaBr for Tower C. If the flashoff losses and the loss due to formation of organobromine species are not accounted for, the appropriate composition would mistakenly be calculated as only 0.35% NaBr for Tower A, 0.22% NaBr for Tower B and 0.19% for Tower C.

45

-54-

If chlorine gas is being used as the hypochlorite donor, then the second to last line in Table 4B gives the amount of sodium bromide that must be added separately to maintain the optimum Conversion Ratio in the recirculating
5 water.

Example 8 - Determination of an Appropriate Hypochlorite Donor/Bromide Ion Donor Biocide Composition.

10 This example demonstrates why understanding of bromide ion loss phenomena is critical to development of commercial biocides containing both hypochlorite donors and bromide ion donors.

15 In this example, a cooling tower system with a recirculating water capacity of 100,000 gallons is treated with ACL90 PLUS to maintain a free available chlorine concentration of 0.5 mg/L (0.5 ppm) in the water. The daily available chlorine demand is satisfied with 11.0
20 pounds of ACL90 PLUS. Since the available chlorine content of ACL90 PLUS is 90.7%, 11.0 pounds of ACL90 PLUS tablets per day are equivalent to 10.0 pounds of available chlorine ($11.0 \times 0.907 = 10.0$).

25 The ACL90 PLUS chlorine biocide can be made to perform as a bromine biocide by adding sufficient sodium bromide to the water to maintain a Conversion Ratio of at least 1.0. This requires maintenance of a bromide ion concentration in the cooling water sufficient to satisfy
30 the stoichiometric requirements of equations (6a) and (6b). Hence, the bromide ion concentration must be 0.56 ppm ($0.5 \text{ ppm of } Cl_2 \times M_{Br}/M_{Cl_2} = 0.5 \times 79.909/70.906 = 0.56$). Since the recirculating water in the example cooling tower weighs 834,000 pounds (100,000 gallons x
35 8.34 pounds/gallon), it must contain at least 0.47 pounds of bromide ion ($0.56 \times 10^{-6} \times 834,000 \text{ pounds} = 0.47$

-55-

pounds). This requires that the water contain a minimum of 0.605 pound of sodium bromide ($0.47 \text{ pound} \times \frac{M_{\text{NaBr}}}{M_{\text{Br}}} = 0.47 \times 102.90/79.909 = 0.605$).

5 To make an ACL90 PLUS/NaBr composition perform as a bromine biocide, the composition must contain sufficient sodium bromide to build the bromide ion concentration up to and maintain it at the level required to satisfy the optimum Conversion Ratio. This can be achieved by knowing
10 the bromide ion loss rates for the recirculating water system. If the ACL90 PLUS/NaBr product contains the exact amount of sodium bromide to compensate for the losses and maintain the Conversion Ratio at exactly one, then the sodium bromide concentration will automatically change
15 with time until the desired concentration is reached. This occurs as follows:

When feeding a NaBr/ACL composition to a tower which initially contains no bromide ion, the bromide ion
20 concentration will increase. The bromide ion loss rate depends on the concentration, so that the loss rate at low concentrations is very small, but slowly increases as the concentration of bromide ion increases. Thus, the initial bromide ion addition rate is larger than the bromide ion
25 loss rate and the bromide ion concentration increases. This continues until the bromide ion loss rate matches the rate at which bromide ion is added to the system. At this point, a dynamic equilibrium condition, commonly referred to as a steady state, has been reached. Under these
30 conditions, the bromide ion loss rate is equal to the rate at which bromide ion is being added and no further change in the bromide ion content occurs. If the hypochlorite donor/bromide ion donor composition contained the exact amount of bromide ion to compensate for bromide ion losses
35 at the desired steady state, that is the steady state which is eventually attained.

-56-

On the other hand, if the tower initially contains an excess of NaBr over the amount required for a Conversion Ratio of 1.0 and a NaBr/ACL mixture is used that corresponds to the desired steady state concentration, the bromide ion loss rate will be higher than the bromide addition rate. In this case, the bromide ion concentration will decrease until the loss rate and addition rate are equal and a steady state at Conversion Ratio = 1.0 is reached. Again, this steady state is determined by the bromide ion addition rate, and, if the correct composition is used, the Conversion Ratio will be one at steady state.

This concept can best be visualized by considering the following information. First, in the preceding Example, 11.0 pounds of ACL90 PLUS are required to satisfy the daily chlorine demand of the cooling water. Second, 0.605 lb of sodium bromide are required to maintain the desired Conversion Ratio of 1.0. It follows that the total daily requirements for the hypochlorite donor/bromide ion donor composition, (ACL 90 PLUS/NaBr) are 11.605 pounds ($11.0 + 0.605$). The appropriate composition of the hypochlorite donor/bromide ion donor composition required to maintain the desired Conversion Ratio is, therefore, 94.8% ($11.0/11.605 \times 100\% = 94.8\%$) ACL90 PLUS and 5.2% ($0.605/11.605 \times 100\% = 5.2\%$) NaBr.

To understand how this composition can build up the bromide ion concentration to the desired level, it is necessary to consider the bromide ion addition rate and total bromide ion loss rate on an hourly basis. Again, as shown above, the total weight of bromide ion, W_{Br} , required to maintain the Conversion Ratio at 1.0 was established to be 0.47 lb at steady state. For the purpose of this Example, it is assumed that this will be the total amount of bromide ion that is lost daily. Then

-57-

the total hourly bromide ion loss rate (all pathways), HTBrL, is simply W_{Br} divided by 24 hours. This corresponds to a rate of 0.01958 lb/hr ($0.47 \text{ lb} \div 24 \text{ hr} = 0.01958$). With respect to W_{Br} , the percent total hourly bromide ion loss rate, PHTBrL is, as determined by equation (25), 4.2% ($0.01958/0.47 \times 100\% = 4.2\%$).

$$\text{PHTBrL} = \frac{\text{HTBrL}}{W_{Br}} \times 100\% \quad (25)$$

This percent total hourly loss rate corresponds to a percent total daily loss rate of 100%. It is important to remember that it is entirely possible for percent total daily loss rate to be greater than 100%.

With regards to the bromide ion addition rate, it was established previously that 0.605 lb of sodium bromide are required to satisfy the Conversion Ratio conditions specified. The hourly sodium bromide addition rate is thus 0.02521 lb/hr ($0.605 \text{ lb} \div 24 \text{ hr}$). In terms of bromide ion, the total hourly addition rate is 0.01958 lb/hr ($0.02521 \text{ lb NaBr/hr} \times M_{Br}/M_{NaBr} = 0.02521 \times 80/103 = 0.01958$).

It follows that at the end of the first hour of use of the ACL90 PLUS/NaBr composition the bromide ion content of the water will be 0.01958 pounds minus the amount of bromide ion losses. Since the total hourly loss rate is 4.2%/hr, the amount of bromide ion lost in the first hour is only 0.00082 lb (0.042×0.01958). The bromide ion content at the end of the first hour is thus 0.01876 lb ($0.01958 - 0.00082$). At the end of the second hour, another 0.01958 lb of bromide will have been added bringing the gross amount to 0.03834 ($0.01876 + 0.01958$) lb. However, the bromide ion loss is slightly higher and amounts to approximately 0.00161 lb (0.03834×0.0420).

-58-

The net amount of bromide ion remaining has now increased to 0.03673 lb (0.03834 - 0.00161). Thus, with each successive addition of sodium bromide, the bromide ion concentration will continue to increase, but at the same time, the bromide ion loss rate will increase. Eventually, the loss rate will catch up with the addition rate and the two rates will be essentially equivalent thereafter. At this point, steady state conditions have been attained and subsequent ACL90 PLUS/NaBr additions merely maintain the Conversion Ratio at the desired level, in this case, 1.0

A further refinement of these calculations is to determine the hourly bromide ion losses by the various pathways, since blowdown losses apply to all bromine species but losses by flashoff of hypobromous acid and bromamines and the formation of organobromine compounds apply only to the hypobromite species. This is achieved with equations (26) and (27). The percent hourly bromide ion loss rate by blowdown, PHBrL(BD), is calculated by equation (26).

$$\text{PHBrL(BD)} = \frac{\text{BrL(BD)}}{C_{\text{Br}} \times V_w} \times \frac{1000}{24} \times 100\% \quad (26)$$

where: PHBrL(BD) = the percent of bromide ion lost by blowdown, %/hr

BrL(BD) = as defined in equation (9)

C_{Br} = as defined in step (3) of "calculation of losses method"

V_w = volume of recirculating water, L

1000 = conversion factor, grams to milligrams

24 = conversion factor, days to hours

The percent hourly loss of bromide ion by the other pathways (flashoff of hypobromous acid and bromamines and

-59-

formation of organobromine compounds) is specifically proportional to the amount of hypobromite species in the recirculating water. The percent hourly loss of hypobromite species by these pathways, PHOBrL, is calculated with equation (27).

(27)

$$\text{PHOBrL} = \frac{[\text{TBrL} - \text{BrL(BD)}]}{C_{\text{HOBr}} \times V_w} \times \frac{M_{\text{HOBr}}}{M_{\text{Br}}} \times \frac{1000}{24} \times 100\%$$

where: PHOBrL = percent of hypobromite species lost by pathways other than blowdown, %/hr

TBrL = as defined in equation (23)

BrL(BD) = as defined in equation (9)

C_{HOBr} = as defined in step (2) of "calculation of losses method"

V_w = volume of recirculating water, L

M_{HOBr} = mole weight of hypobromous acid, gm

M_{Br} = mole weight of bromide ion, gm

1000 = conversion factor, grams to milligrams

24 = conversion factor, days to hours

PHOBrL is essentially the weight of hypobromite species lost per hour divided by the weight of hypobromite species contained in the recirculating water. With equation (25), the percent total hourly bromide ion loss rate, PHTBrL, was calculated to be 4.2%/hr. These refinements account for what fraction of bromide ion losses are due to blowdown and the other pathways. To illustrate the refinements of the calculations, the losses due to blowdown, PHBrL(BD), and the losses by other pathways, PHOBrL, are taken to be 0.83%/hr and 3.33%/hr, respectively, for Figures 2-5.

-60-

These calculations can be used to illustrate the interrelationship between the concentration of the bromide ion in the recirculating water and the composition of the hypochlorite donor/bromide ion donor compositions. They were utilized to generate the graphs shown in Figures 2-5 which illustrate the effect of the biocide composition on the buildup of bromide ion with time and the ability of the composition to attain the optimum Conversion Ratio at steady state conditions. Since these calculations simulate the dynamics of the bromide ion content of water recirculation systems, they can be used to determine the composition required to produce the desired Conversion Ratio once the PHBrL(BD) and PHOBrL have been determined. Figure 6 illustrates the effect of bromide ion loss rate on the composition required for the preferred range of Conversion Ratios. Therefore, it illustrates, in conjunction with the following examples, how the various compositions are able to perform as bromine biocides.

20

Example 9 - Buildup of Bromide Ion to Steady State Concentration with a 2% NaBr/98% ACL90 PLUS Composition.

The cooling tower in Example 8 is initially treated with 11.0 pounds of ACL90 PLUS per day to maintain a free chlorine concentration of 0.5 mg/L, thus the tower initially contains no bromine containing species. The biocide is then switched to a composition of 2% NaBr and 98% ACL90 PLUS. Figure 2 presents the calculated bromide ion content in terms of sodium bromide of the tower versus the time elapsed since starting the NaBr/ACL90 PLUS composition, given that PHOBrL = 3.33%/hour (80%/day) and that PHBrL(BD) = 0.83%/hour (20%/day). It shows how the total amount of bromine containing species (given as pounds of NaBr) contained in the recirculating water system builds up with time during the initial few days of

-61-

use of the 2.0% NaBr/98% ACL90 PLUS composition until a steady state concentration is reached after about three days. At steady state, the tower in Figure 2 contains about 0.2 pounds of NaBr, which is considerably below the 5 0.605 pounds of NaBr required for a Conversion Ratio of 1.0, as shown by the line labeled "CR = 1.0". In this case, the free halogen is a mixture of hypochlorite species and hypobromite species and the killing efficiency is less than ideal.

10

Example 10 - Buildup of Bromide Ion to Steady State Concentration with a 9% NaBr/91% ACL90 PLUS composition.

Figure 3 shows the case where a 15 NaBr/trichloroisocyanuric acid (ACL90 PLUS) composition with a much higher percentage of NaBr (9.0%) is fed into the tower described in Example 8. As in Example 9, the bromide ion content of the tower builds up smoothly until a steady state is reached. In this case, however, steady 20 state is reached in about 20 days. The steady state NaBr content is 3.0 pounds and the steady state Conversion Ratio is 5.0. In this case, all of the free halogen is present as hypobromite species and the killing efficiency is very high, but a considerable excess of bromide ion is 25 present which is wasted.

Example 11 - Buildup of Bromide Ion to Steady State Concentration with the Optimum 5.2% NaBr/94.8% ACL90 PLUS Composition.

30

Figure 4 shows the ideal case for the tower described in Example 8, where PHBrL(BD) is 0.83%/hour (20%/day) and PHOBrL is 3.33%/hour (80%/day). A Conversion Ratio of 1.0 is achieved after about three days and then maintained at 35 steady state conditions by feeding a composition of 5.2% NaBr/94.8% trichloroisocyanuric acid. This composition

-62-

therefore performs as a bromine biocide in this tower with very little excess bromide ion being required.

Example 12 - Buildup of Bromide Ion to Steady State
Concentration with BCDMH

Figure 5 shows the case for BCDMH, which has a bromide and available halogen content equivalent to about 40% NaBr/60% trichloroisocyanuric acid, in the tower of Example 8. The steady state Conversion Ratio (for $\text{PHOBrL} = 3.33\%/ \text{hour}$ and $\text{PHBrL(BD)} = 0.83\%/ \text{hour}$) which is attained after about 20 days is 56.7. This is a tremendous waste of bromide ion, since 56.7 times as much bromide is used as is necessary to maintain the maximum killing efficiency. This high Conversion Ratio for BCDMH is confirmed by the data in Example 1, Table 1, where a Conversion Ratio of 41.1 was determined experimentally for BCDMH in a tower with somewhat different characteristics. The waste of bromide is even greater for cases where PHOBrL and PHBrL(BD) are lower than used in this example.

Example 13 - Hypochlorite Donor/Bromide Ion Donor
Compositions Required For Specific Steady
State Conversion Ratios

The relationship between the sum of PHBrL(BD) and PHOBrL and the required composition of a NaBr/trichloroisocyanuric acid (ACL90 PLUS) composition is summarized in Figure 6. The line labeled 'CR = 1.0' gives the relationship between $\text{PHBrL(BD)} + \text{PHOBrL}$ and the weight % NaBr required in the composition to produce a Conversion Ratio of 1.0. For instance, for a tower with a bromide ion loss rate of 3.3%/hour the NaBr/trichloroisocyanuric acid composition should be 4.8% NaBr. The lines marked 'CR = 4.0' and 'CR = 0.5' give the relationship for the extremes of the most preferred Conversion Ratio. The

-63-

dashed arrow at 4% NaBr shows that a composition of 4% NaBr/96% trichloroisocyanuric acid can maintain the Conversion Ratio in the most preferred range of 0.5 to 4.0 for towers for PHBrL(BD) + PHOBrL = 0.75%/hour to well over 5%/hour. This range covers virtually all common cooling tower systems. In contrast, a composition with only 2% NaBr/98% trichloroisocyanuric acid will maintain the Conversion Ratio in the most preferred range only for PHBrL(BD) + PHOBrL between 0.38 and 2.5%/hour. Many common cooling towers have larger bromide ion loss rates than this, as was shown in Examples 3 and 4.

This example shows the importance of understanding the relationship between the total bromide ion loss rate and the sodium bromide content of ACL90 PLUS/NaBr compositions and the capabilities of these compositions to attain and maintain the desired Conversion Ratios, especially those that enable these compositions to perform as bromine biocides. These same relationships also exist for other hypochlorite donor/bromide ion donor compositions and/or combinations. These relationships can be established with the methods described herein.

For cooling tower operations subject to EPA discharge limits of 0.2 ppm (available chlorine basis), it is preferred to maintain the Conversion Ratio at or above one, since hypobromite species dissipate faster than hypochlorite species.

For use in air washers, it is preferred that the Conversion Ratio be maintained at or above a value of one since it is important to eliminate all chlorine or chloramine odors from the air passed through the air washer. Odor is more important in air washers than in cooling towers since the washed air is used inside buildings, factories, and the like. Thus, somewhat higher

-64-

percentages of NaBr are required for compositions of this invention used in cooling tower operations subject to EPA limits and in air washers. For instance, Figure 6 shows that a 4% NaBr/96% trichloroisocyanuric acid composition will maintain the Conversion Ratio in the preferred range of 1.0 to 4.0 for $\text{PHBrL(BD)} + \text{PHOBrL} = 0.75\%$ to 2.75%/hour. If the loss rate is higher, a composition with a higher NaBr percentage would be necessary.

10

Example 14 - Demonstration of Bromide Ion Loss From Spas

This example demonstrates the magnitude of bromide ion loss that can occur in a commercial spa. A spa with a capacity of 1000 gallons of water was chlorinated continuously with ACL90 PLUS (trichloroisocyanuric acid) around the clock to maintain a free chlorine concentration of 2 ppm. The spa water was maintained at a temperature of 40°C. The water was aerated only during the day, the high bather load period, for about 12 hours. Sufficient sodium bromide was added to the spa water to obtain a bromide ion concentration of 3 ppm. This is the amount required to attain a Conversion Ratio of 1.33 versus the optimum of 1.0 and to make the chemicals perform as a bromine sanitizer. Water samples were taken about every four hours for several days. The analyses showed that the bromide ion concentration decreased steadily from 3 to 1 ppm over a period of 6 days. The chlorine demand was about 10 ppm per day (available chlorine basis). During this period, the odor of the air above the spa changed gradually from that of bromamines to chloramines. These results demonstrated that bromide ion was lost from the water and that the hypohalite species were a mixture of hypochlorite and hypobromite species. As a consequence, the biocide performed more like a chlorine sanitizer than a bromine sanitizer.

-65-

Example 15 - Control of Optimum Conversion Ratio in Spas
with ACL90 PLUS/NaBr Compositions

This example further demonstrates how knowledge of
5 the bromide ion loss can be applied to the development of
the appropriate sanitizer compositions. The results in
Example 14 show that the bromide ion loss rate was about
0.33 ppm/day. This means that at least 2.5 grams must be
added daily to maintain the desired concentration. The
10 chlorine demand during this period was about 10 ppm/day,
which corresponds to a ACL90 PLUS consumption rate of 41.3
grams/day. These results indicate that to satisfy the
chlorine demand and bromide ion loss requirements with a
product made of the two materials, the product must
15 contain ACL90 PLUS and sodium bromide in the weight
proportions of 41.3 to 2.5. Thus, the tablet for this
application must contain at least 94.3 wt % ACL90 PLUS and
5.7 wt % sodium bromide.

20 To demonstrate the utility of this concept, an ACL90
PLUS/sodium bromide mixture with 6% NaBr was compacted
into one-inch tablets weighing 15 grams each. The tablets
were placed in a standard erosion feeder where the water
flow was adjusted to maintain the desired free halogen
25 concentration of 2 ppm (available chlorine basis). Water
samples were then taken periodically for six days. The
bromide analyses showed that the bromide ion concentration
built up steadily to the desired concentration and
remained constant for the remainder of the test, thereby
30 insuring that this product was performing as a bromine
sanitizer.

-66-

Bromine Volatilization Suppressant

It has also been discovered that, in addition to simply adding enough bromide ion donor to compensate for all bromide ion losses, it is possible to approach the problem in a second way, that is, by reducing or suppressing the amount of volatilization of HOBr and bromamines. This can be accomplished by addition of a hypobromous acid volatilization suppressant compound. The volatilization suppressant must bind free bromine species (HOBr) strongly enough to reduce the concentrations of hypobromous acid and bromamine significantly, but not so strongly that the disinfecting properties of the bromine-based biocide will be reduced. In addition, the volatilization suppressant must be chemically compatible with the hypochlorite donor compounds in the single product compositions to be fed to the tower.

Cyanuric acid has been used in swimming pools to reduce the decomposition of hypochlorous acid by the UV rays of sunlight and in cooling towers to reduce the loss of free chlorine. However, cyanuric acid will not suppress the loss of free bromine by volatilization and degradation in sunlight because cyanuric acid does not bind free bromine as strongly as it does free chlorine.

It has been found that hydantoin derivatives (such as DME); sulfonamide derivatives; sulfamic acid derivatives; glycoluril derivatives; oxazolidinone derivatives; imidazolidinone derivatives; and succinimide derivatives are capable of acting as volatilization suppressants for free bromine. However, it was discovered that when hydantoin derivatives are used, the concentration of the volatilization suppressant relative to the concentration of the free bromine must be controlled in order to avoid

-67-

significant reduction in the biocidal activity of the biocides of the present invention.

DMH can be used to reduce bromide ion losses by
5 reducing volatilization loss by as much as 85% before it begins to have a deleterious effect on the disinfection properties of the bromine-based biocide according to the present invention. However, DMH concentrations more than
10 ten times the hypobromous acid concentration (expressed in terms of free available chlorine) can significantly decrease the biocidal effectiveness of the hypobromous acid. For example, if the free halogen level in the recirculating water is controlled at 0.5 mg/L (free
15 available chlorine basis), DMH concentrations greater than 5.0 mg/L must be avoided. DMH concentrations of over 50 mg/L can easily be reached if BCDMH is used as the biocide. Because of the potential for reducing the effectiveness of bromine-based biocides, the concentration
20 of DMH or other stabilizer compounds should be maintained at an appropriately low level, preferably less than 10 ppm in the case of DMH.

25 Example 16 - Demonstration of the Effect of
Dimethylhydantoin on Bromide Ion Losses

This example demonstrates how bromide ion losses can be significantly reduced with bromine volatilization suppressants.

30

In this particular experiment, the cooling water of Example 4 was dosed with enough sodium bromide to obtain a Conversion Ratio of about one. DMH was then added to the water in an amount sufficient to attain a concentration of
35 20 ppm. Again, lithium chloride was used as a tracer. The water was recirculated for about one hour to obtain a

-68-

uniform distribution of chemicals. Water samples were then taken periodically for the next 24 hours and analyzed for bromide, lithium and DMH. The results are tabulated in Table 5.

-69-

TABLE 5

Effect of DMH on Bromide Ion Losses

	5	Water Sample	Time Hr.	Bromide Ion Concentration ppm	DMH Concentration ppm	Lithium Concentration ppm	Bromide Ion Losses (%)
		1	1	0.5	21	0.45	0
10		2	2	0.5	20	0.44	0
		3	3	0.5	19	0.42	0
		4	4	0.48	20	0.42	4
		5	8	0.46	20	0.42	8
		6	16	0.42	19	0.41	18
15		7	24	0.38	18	0.42	24

These data demonstrate that bromide ion losses were reduced dramatically with the addition of DMH, thus establishing another way to compensate for bromide ion losses via the volatilization pathway.

Example 17 - Effect of DMH on Henry's Law Constants for Hypobromous Acid

The previous example demonstrated that DMH could be used to obtain significant reductions in bromide ion losses from cooling water systems containing the hypochlorite donor/bromide ion donor compositions described in this invention. This example shows the effect of the DMH concentration on the tendency of the bromide ion to be lost from cooling waters by volatilization. Just as important, it provides data critical to controlling the DMH concentration so that the excellent biocidal properties of these bromine biocide compositions are not compromised by high DMH residuals.

The effect of DMH concentration was demonstrated by determining the Henry's Law constants for a series of

-70-

solutions in which the available halogen, bromide, pH and temperature were held constant but the DMH concentration was varied.

5 The results of these experiments are tabulated in Table 6 and shown graphically in Figure 7.

Table 6

10

Effect of DMH on Henry's Law Constants For
Solutions Containing Hypohalite Species and
Bromide Ion

15 Experimental Conditions

pH = 8.5

Temperature = 22.5°C

20

Free halogen (as Cl₂) = 2 mg/L

Bromide ion = 2.25 mg/L

25

DMH/Free Bromine
Mole Ratio

Henry's Law Constant
H_k

30

0.0

0.220

2.0

0.037

5.0

0.028

10.0

0.024

30.0

0.019

35 Depicting these results graphically, Figure 7 shows that the Henry's Law constant decreased significantly as the DMH/free bromine mole ratio increased from 0 to 10, but decreased very little above 10. These results indicate that there is no need to use DMH/free bromine ratios of greater than 10. More importantly, killing efficiency data show that the biocidal properties begin to
40 decrease significantly above this ratio.

The foregoing description has been directed to particular embodiments of the invention for the purposes

-71-

of illustration and explanation. It will be apparent, however, to those skilled in this art that many modifications and changes in the compositions and methods set forth will be possible without departing from the scope and spirit of the invention. It is intended that the following claims be interpreted to embrace all such modifications and changes.

-72-

WHAT IS CLAIMED IS:

1. A biocidal composition for use in recirculating water systems comprising a hypochlorite donor and a bromide ion donor, wherein the composition contains an amount of the bromide ion donor effective to maintain a mole ratio of the sum of all bromine containing species to the sum of all hypohalite species in the recirculating water of about 0.2 to about 20.
2. The composition of claim 1 wherein
- the hypochlorite donor is an alkali metal hypochlorite, an alkaline earth metal hypochlorite, a chlorinated hydantoin, a chlorinated oxazolidinone, a chlorinated imidazolidinone, or a chlorinated isocyanuric acid derivative; and
- the bromide ion donor is an alkali metal bromide, an alkaline earth metal bromide, R_4 -ammonium bromide where R is any alkyl or aryl group, a bromamine, a N-brominated hydantoin, a N-brominated sulfonamide, a N-brominated succinimide, a N-brominated oxazolidinone, a N-brominated imidazolidinone, a N-brominated isocyanurate, or a salt of a trihalide or mixed trihalide ion containing bromine.
3. The composition of claim 2 wherein the hypochlorite donor is a chlorinated isocyanuric acid derivative.

-73-

4. The composition of claim 3 wherein the chlorinated isocyanuric acid derivative is sodium dichloro-s-triazinetriene, potassium dichloro-s-triazinetriene, a hydrate of sodium or potassium dichloro-s-triazinetriene,
5 dichloroisocyanuric acid, trichloroisocyanuric acid, [mono(trichloro)-tetra(monopotassium dichloro)]-penta-s-triazinetriene, [mono(trichloro)-mono (monopotassium dichloro)]-di-s-triazinetriene, or mixtures thereof.

10

5. The composition of claim 4 wherein the hypochlorite donor is trichloroisocyanuric acid and the bromide ion donor is sodium bromide or potassium bromide.

15

6. The composition of claim 4 wherein the hypochlorite donor is an alkali metal dichloroisocyanurate and the bromide ion donor is sodium bromide or potassium bromide.

20

7. The composition of claim 1, 2, 3, 4, 5 or 6 comprising:

from about 85 parts by weight to about 99 parts by
25 weight of the hypochlorite donor; and

from about 1 part by weight to about 15 parts by weight of the bromide ion donor.

30

8. The composition of claim 4 wherein the hypochlorite donor is trichloroisocyanuric acid and the bromide ion donor is a brominated hydantoin.

35

-74-

9. The composition of claim 8 wherein the brominated hydantoin is a bromochlorohydantoin.
- 5 10. The composition of claim 2 wherein the hypochlorite donor is a dichlorohydantoin and the bromide ion donor is a bromochlorohydantoin.
- 10 11. The composition of claim 1, 2, 3, 8, 9 or 10 comprising:
- from about 50 parts by weight to about 99 parts by weight hypochlorite donor;
- 15
- from about 1 part by weight to about 50 parts by weight bromide ion donor.
- 20 12. A biocidal composition for use in recirculating water systems comprising a hypochlorite donor, a bromide ion donor, and a bromine volatilization suppressant, wherein the composition contains an amount of the bromide ion donor effective to maintain a mole ratio of the sum of all
- 25 bromine containing species to the sum of all hypohalite species in the recirculating water of about 0.2 to about 20.
- 30 13. The composition of claim 12 wherein:
- the hypochlorite donor is an alkali metal hypochlorite, an alkaline earth metal hypochlorite, a chlorinated oxazolidinone, a
- 35 chlorinated imidazolidinone, or a chlorinated isocyanuric acid derivative;

-75-

- the bromide ion donor is an alkali metal bromide, an alkaline earth metal bromide, R_4 -ammonium bromide where R is any alkyl or aryl group, a bromamine, a N-brominated sulfonamide, a N-brominated succinimide, a N-brominated oxazolidinone, a N-brominated imidazolidinone, a N-brominated isocyanurate, or a salt of a trihalide or mixed trihalide ion containing bromine; and
- the bromine volatilization suppressant is a hydantoin derivative, a sulfonamide derivative, a sulfamic acid derivative, a glycoluril derivative, a succinimide derivative, an oxazolidinone derivative, or an imidazolidinone derivative.

14. The composition of claim 13 wherein the hypochlorite donor is trichloroisocyanuric acid, the bromide ion donor is sodium bromide or potassium bromide, and the bromine volatilization suppressant is dimethylhydantoin.

15. The composition of claim 13 wherein the hypochlorite donor is a alkali metal dichloroisocyanurate, the bromide ion donor is sodium bromide or potassium bromide, and the bromine volatilization suppressant compound is dimethylhydantoin.

16. The composition of claim 12, 13, 14 or 15 comprising:
from about 85 parts by weight to about 98 parts by weight hypochlorite donor;

-76-

from about 1 part by weight to about 15 parts by weight bromide ion donor; and

5 from about 1 part to about 10 parts by weight bromine volatilization suppressant.

17. The composition of claim 12 wherein the hypochlorite donor, the bromide ion donor, and the bromine
10 volatilization suppressant are dry, water-soluble solids.

18. The composition of claim 17 wherein the solids are compacted in the form of tablets, sticks or pucks.
15

19. The composition of claim 18 further comprising a compacting aid.

20

20. The composition of claim 19, wherein the compacting aid is one or more of boric acid, sodium stearate, potassium stearate, aluminum hydroxide, or monoglycerol stearate.

25

21. A method of controlling biofouling and microorganism population levels in recirculating water systems which comprises adding to the system either separately or
30 together in a combination or mixture, an amount of a hypochlorite donor and a bromide ion donor which is effective to maintain a mole ratio of the sum of all bromine containing species to the sum of all hypohalite species dissolved in the recirculating water of about 0.2
35 to about 20.

-77-

22. The method of claim 21 wherein the hypochlorite donor is:

5 gaseous chlorine, an alkali metal hypochlorite, an alkaline earth metal hypochlorite, a chlorinated hydantoin, a chlorinated oxazolidinone, a chlorinated imidazolidinone, or a chlorinated isocyanuric acid derivative; and

10 said bromide ion donor is liquid bromine, bromine chloride, an alkali metal bromide, an alkaline earth metal bromide, R_4 -ammonium bromide where R is any alkyl or aryl group, a bromamine, a N-brominated hydantoin, a N-brominated

15 sulfonamide, a N-brominated succinimide, a N-brominated oxazolidinone, a N-brominated imidazolidinone, a N-brominated isocyanurate, or a salt of a trihalide or mixed trihalide ion containing bromine.

20

23. The method of claim 22 wherein the hypochlorite donor is a chlorinated isocyanuric acid derivative.

25

24. The method of claim 23 wherein the chlorinated isocyanuric acid derivative is sodium dichloro-s-triazinetriene, potassium dichloro-s-triazinetriene, a hydrate of sodium or potassium dichloro-s-triazinetriene,

30 dichloroisocyanuric acid, trichloroisocyanuric acid, [mono(trichloro)-tetra(monopotassium dichloro)]-penta-s-triazinetriene, [mono(trichloro)-mono(monopotassium dichloro)]-di-s-triazinetriene, or mixtures thereof.

35

-78-

25. The method of claim 24 wherein the hypochlorite donor is trichloroisocyanuric acid and the bromide ion donor is sodium bromide or potassium bromide.

5

26. The method of claim 24 wherein the hypochlorite donor is an alkali metal dichloroisocyanurate and the bromide ion donor is sodium or potassium bromide.

10

27. The method of claim 21, 22, 23, 24, 25 or 26 wherein said mixture comprises;

from about 85 parts by weight to about 99 parts by weight of a hypochlorite donor; and

from about 1 part by weight to about 15 parts by weight of a bromide ion donor.

20

28. The method of claim 24 wherein the hypochlorite donor is trichloroisocyanuric acid and the bromide ion donor is a brominated hydantoin.

25

29. The method of claim 28 wherein the brominated hydantoin is bromochlorohydantoin.

30

30. The method of claim 22 wherein the hypochlorite donor is a dichlorohydantoin and the bromide ion donor is a bromochlorohydantoin.

35

31. The method of claim 21, 22, 23, 28, 29 or 30 wherein said mixture or combination comprises:

-79-

from about 50 parts by weight to about 99 parts by weight hypochlorite donor; and

5 from about 1 part by weight to about 50 parts by weight bromide ion donor.

32. A method of controlling biofouling and microorganism population levels in recirculating water systems which
10 comprises adding to the system, separately or together in a combination or mixture, an amount of a hypochlorite donor, a bromide ion donor, and a bromine volatilization suppressant which is effective to maintain a mole ratio of the sum of all bromine containing species to the sum of
15 all hypohalite species dissolved in the recirculating water of about 0.2 to about 20.

33. The method of claim 32 wherein:
20

the hypochlorite donor is gaseous chlorine, an alkali metal hypochlorite, an alkaline earth metal hypochlorite, a chlorinated oxazolidinone, a chlorinated imidazolidinone, or a chlorinated
25 isocyanuric acid derivative;

the bromide ion donor is liquid bromine, bromine chloride, an alkali metal bromide, an alkaline earth metal bromide, R_4 -ammonium bromide where R
30 is any alkyl or aryl group, a bromamine, a N-brominated sulfonamide, a N-brominated succinimide, a N-brominated oxazolidinone, a N-brominated imidazolidinone, a N-brominated isocyanurate, or a salt of a trihalide or mixed
35 trihalide ion containing bromine; and

-80-

the bromine volatilization suppressant is a hydantoin derivative, a sulfonamide derivative, a sulfamic acid derivative, a glycoluril derivative, a succinimide derivative, an oxazolidinone derivative, or an imidazolidinone derivative.

34. The method of claim 33 wherein the hypochlorite donor is trichloroisocyanuric acid, the bromide ion donor is sodium bromide or potassium bromide, and the bromine volatilization suppressant is dimethylhydantoin.

35. The method of claim 33 wherein the hypochlorite donor is an alkali metal dichloroisocyanurate, the bromide ion donor is sodium bromide or potassium bromide and the bromine volatilization suppressant is dimethylhydantoin.

36. The method of claim 32, 33, 34 or 35 wherein said mixture or combination comprises:

from about 85 parts by weight to about 99 parts by weight hypochlorite donor;

from about 1 part by weight to about 15 parts by weight bromide ion donor; and

from about 1 part to about 15 parts bromine volatilization suppressant.

37. The method of claim 32 wherein the hypochlorite donor, the bromide ion donor and the bromine volatilization suppressant are dry, water-soluble solids.

-81-

38. The method of claim 37 wherein the solids are compacted in the form of tablets, sticks or pucks.

5 39. The method of claim 38 wherein the mixture or combination further comprises a compacting aid.

40. The method of claim 39 wherein the compacting aid is
10 one or more of boric acid, sodium stearate, potassium stearate, aluminum hydroxide, or monoglycerol stearate.

41. The method of claim 21 wherein the mixture or
15 combination is introduced into the recirculating water system by any of the following means: an erosion feeder, a floater, porous bags, perforated buckets or hand dosing.

20 42. The method of claim 21 further comprising the step of introducing an effective amount of one or more scale inhibitors into the recirculating water.

25 43. The method of claim 42 wherein the scale inhibitor is included in the mixture of hypochlorite donor and bromide ion donor.

30 44. The method of claim 43 wherein the scale inhibitor is one or more of polymaleic acid, polyacrylic acid, a phosphonate, or a polyphosphate.

-82-

45. The method of claim 21 wherein the recirculating water system is an air washer, swimming pool or spa and said ratio is at least 1.

5

46. A method of controlling biofouling and microorganism population levels in a recirculating water system which comprises adding a hypochlorite donor and a bromide ion donor to the system in quantities sufficient to form and
10 maintain hypobromous acid in the system, the quantity of bromide ion donor being sufficient to compensate for losses of bromide ion from the system due to blowdown, volatilization of bromine compounds from the system, and formation of stable organobromine compounds.

15

47. A method of maintaining a concentration hypobromous acid in a recirculating water system sufficient to reduce the microorganism population in the system to a desired
20 level which comprises:

ascertaining the chlorine demand of the system and the rate of bromide ion loss from the system due to blowdown, volatilization, and formation of
25 stable organobromine compounds; and

adding a hypochlorite donor and a bromide ion donor to the system in quantities sufficient to provide said concentration of hypobromous acid
30 in the system and maintain a mole ratio of the sum of all bromine containing species to the sum of all hypohalite species of about 0.2 to about 20.

1/7

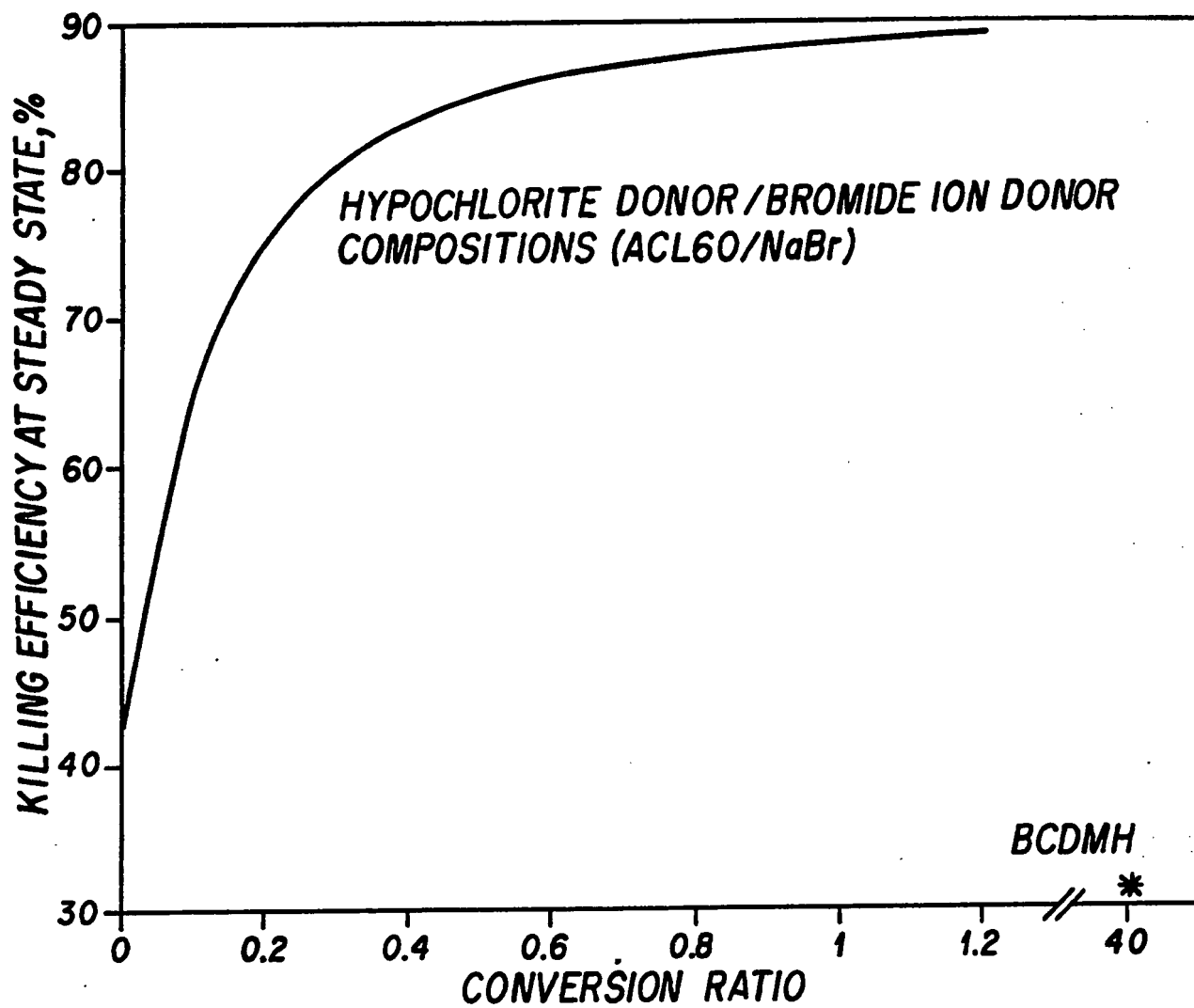


FIG. 1

2/7

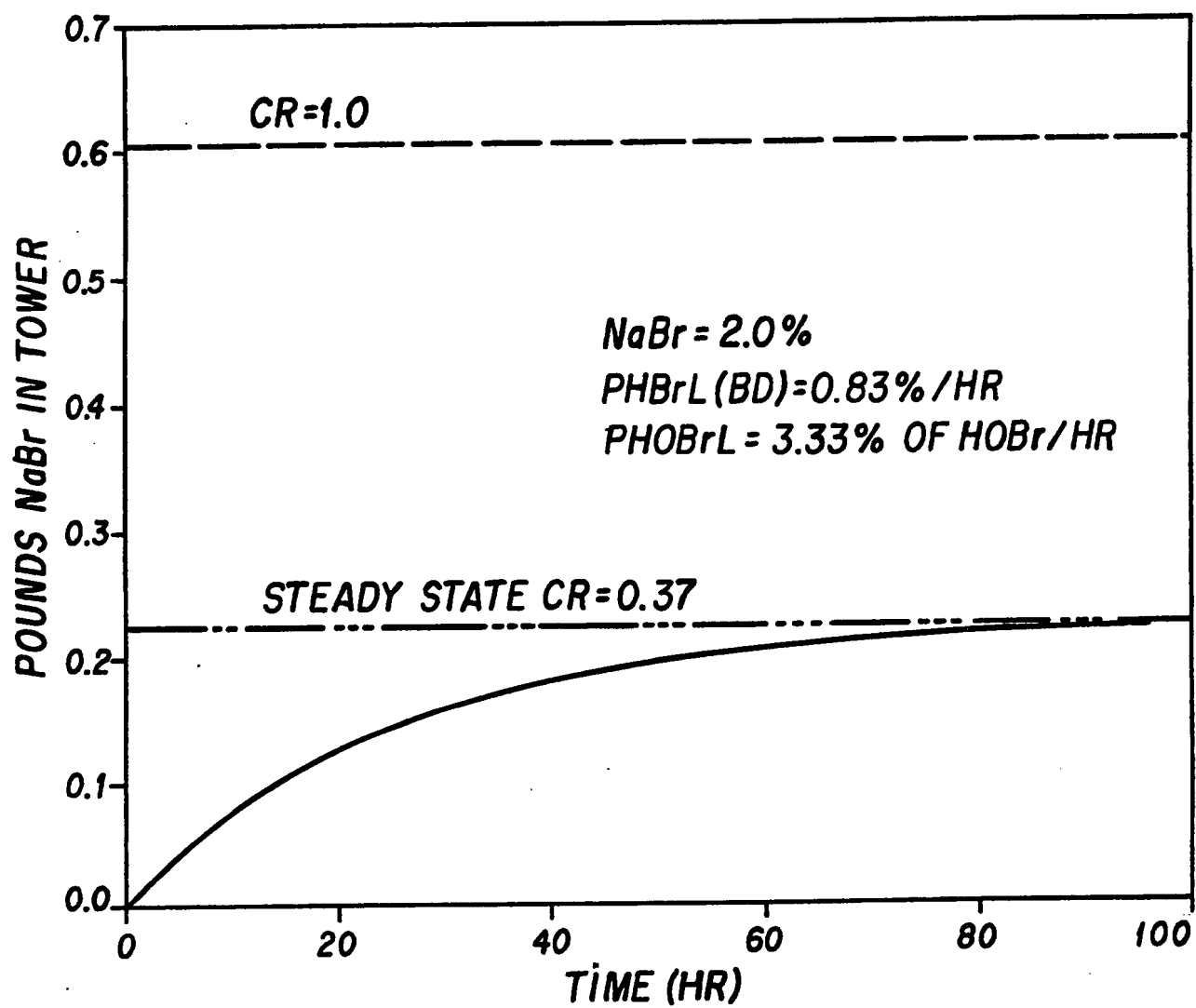


FIG. 2

3/7

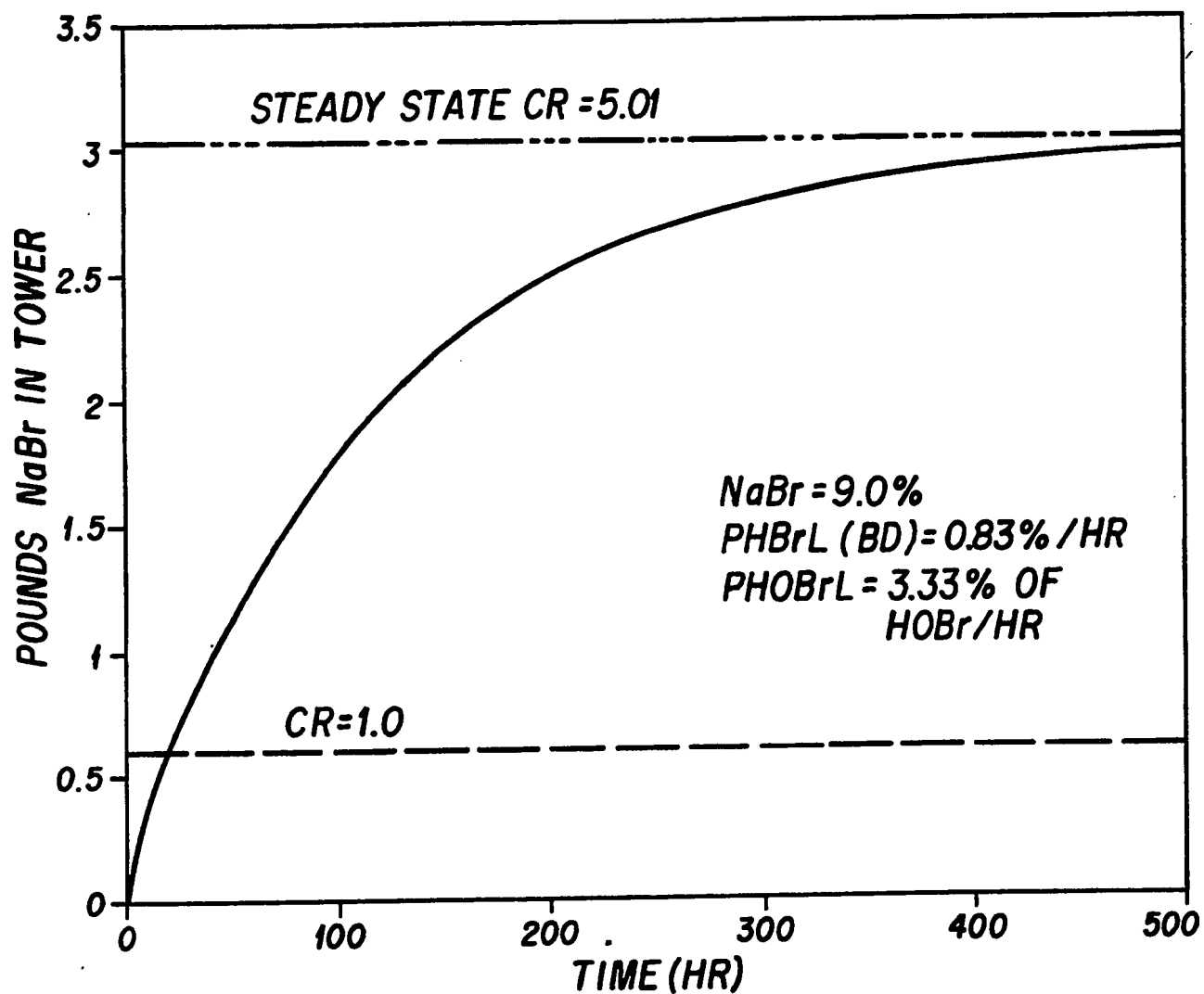


FIG. 3

4/7

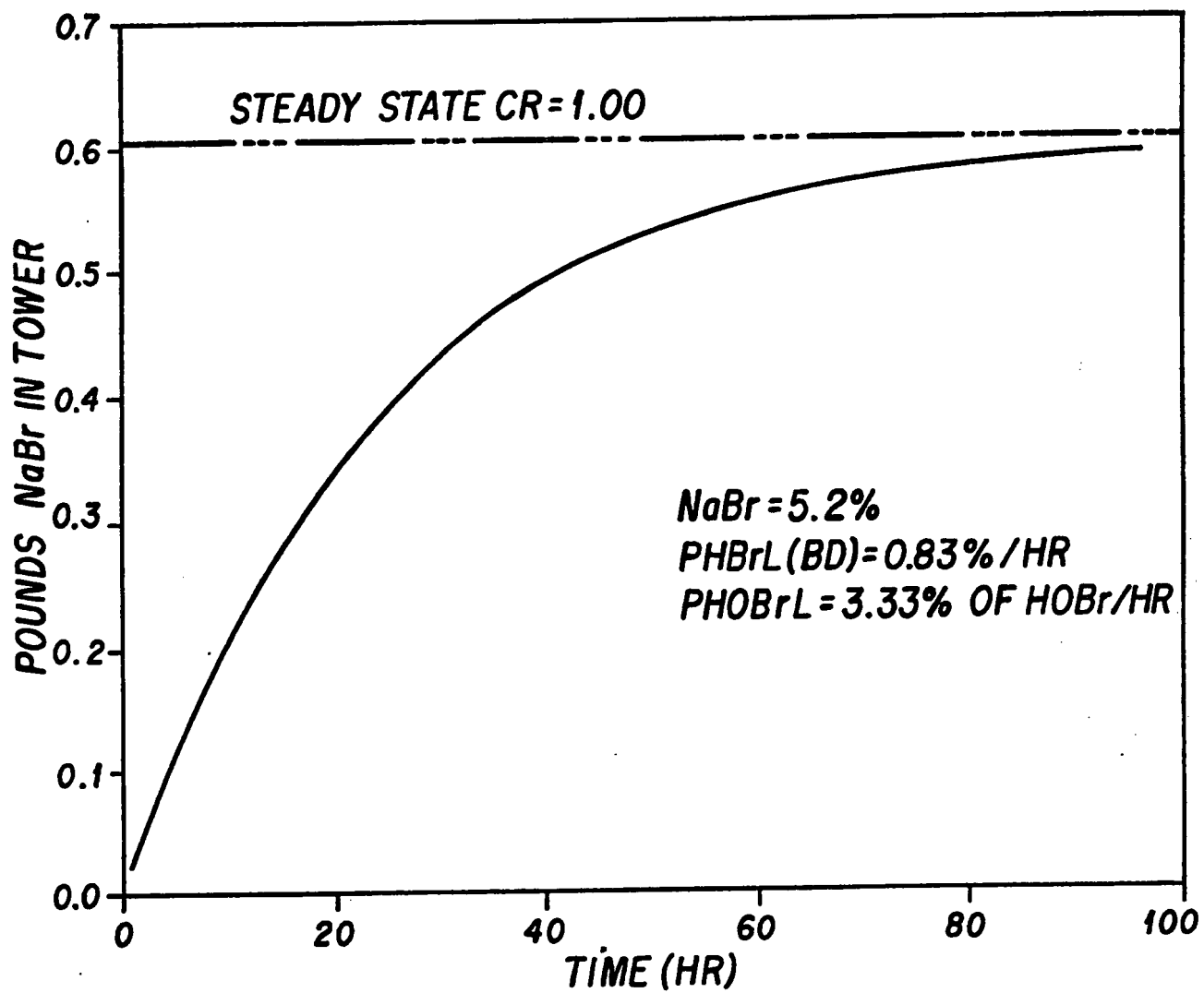


FIG. 4

5/7

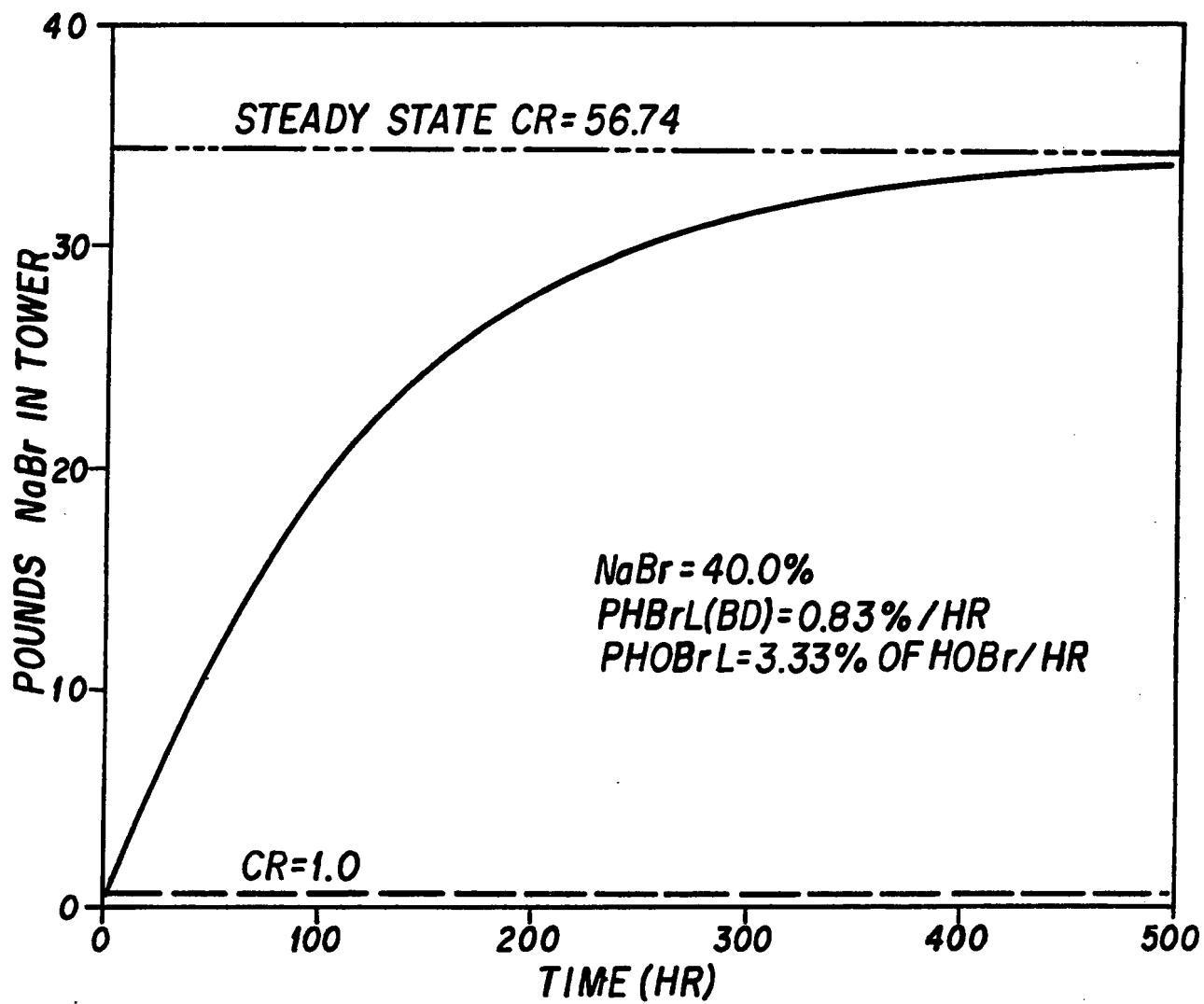


FIG. 5

6/7

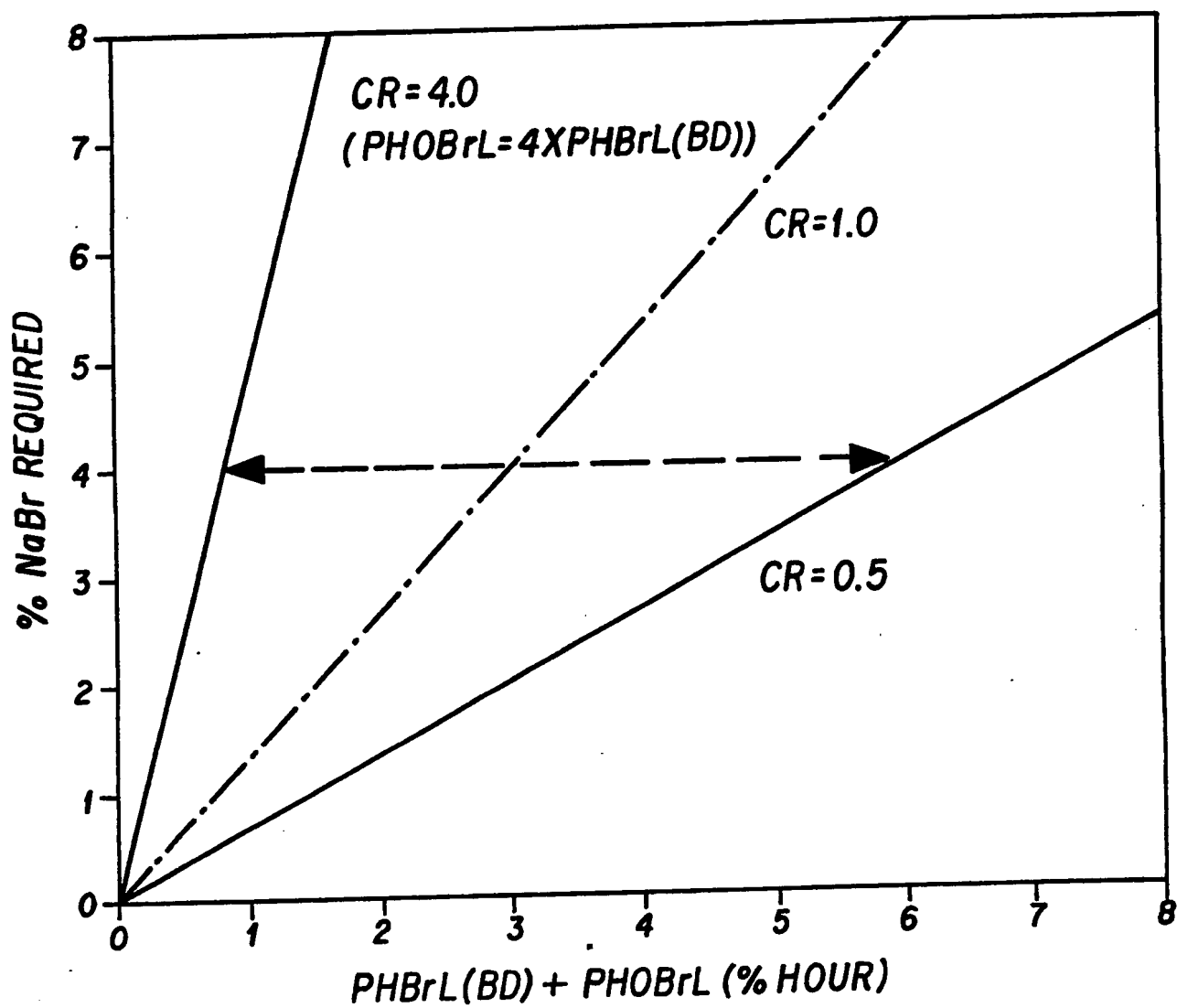


FIG. 6

7/7

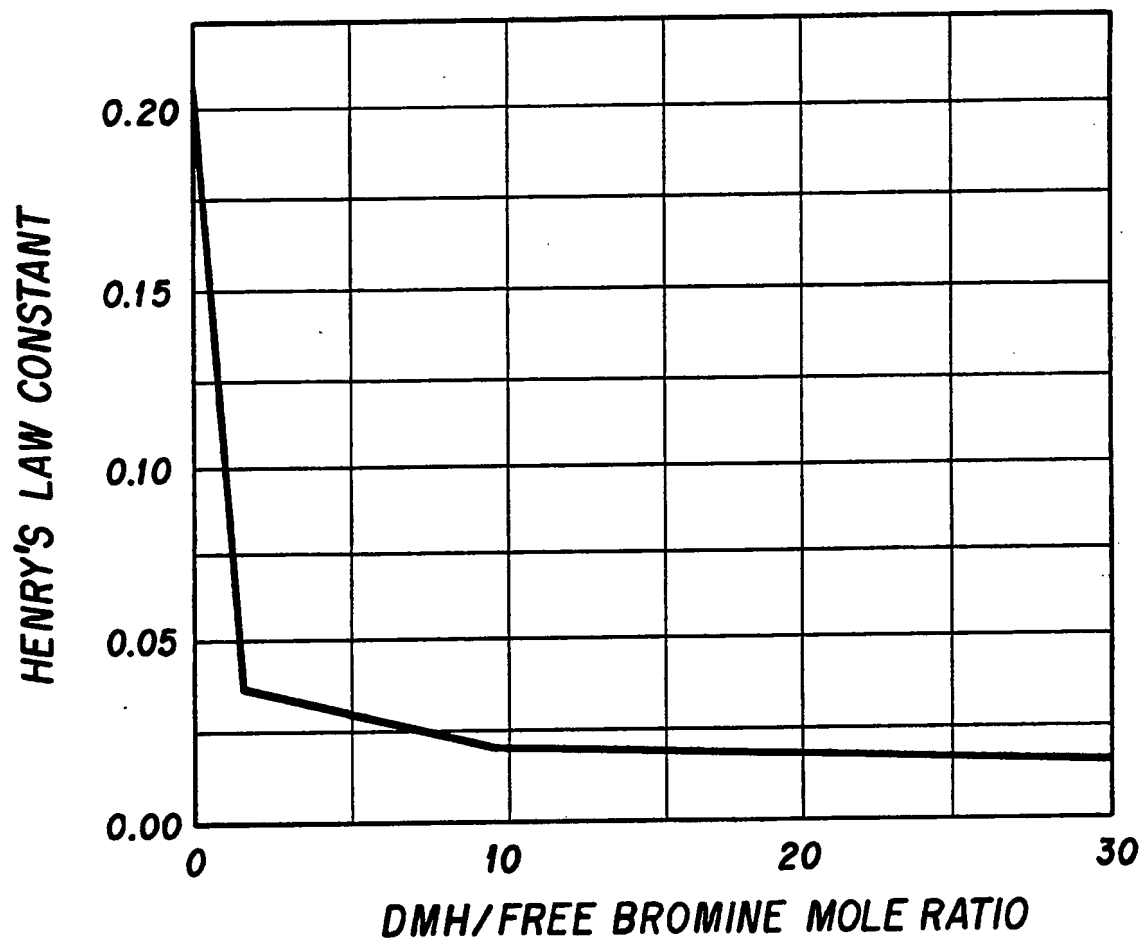


FIG. 7

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/03139

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 02 F 1/76, 1/50, 5/08																				
II. FIELDS SEARCHED <div style="text-align: right; font-size: small;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border-bottom: 1px solid black; font-size: small;">Classification System</td> <td style="border-bottom: 1px solid black; font-size: small;">Classification Symbols</td> </tr> <tr> <td style="padding: 10px 5px;">IPC⁵</td> <td style="padding: 10px 5px;">C 02 F, A 01 N</td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁵	C 02 F, A 01 N														
Classification System	Classification Symbols																			
IPC ⁵	C 02 F, A 01 N																			
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse; font-size: small;"> <thead> <tr> <th style="width: 10%;">Category ¹⁰</th> <th style="width: 70%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>US, A, 4759852 (M.G. TRULEAR) 26 July 1988 see the whole document <div style="text-align: center;">--</div></td> <td style="vertical-align: top;">1-2,5-7,11- 13,16,21-22, 27,32-33,36, 42-44,46-47</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>FR, A, 1126432 (DIVERSEY CORP.) 22 November 1956 see the whole document <div style="text-align: center;">--</div></td> <td style="vertical-align: top;">1-2,5,7,10- 11,17-18,21, 25-27,31</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>US, A, 2815311 (J.G. ELLIS et al.) 3 December 1957 see the whole document (cited in the application) <div style="text-align: center;">--</div></td> <td style="vertical-align: top;">1-7,11,17- 18,21,42- 44</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>US, A, 4698165 (T.W. THEYSON) 6 October 1987 see the whole document <div style="text-align: center;">--</div></td> <td style="vertical-align: top;">1,21-22</td> </tr> <tr> <td colspan="3" style="text-align: center; padding-top: 10px;">./.</td> </tr> </tbody> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	US, A, 4759852 (M.G. TRULEAR) 26 July 1988 see the whole document <div style="text-align: center;">--</div>	1-2,5-7,11- 13,16,21-22, 27,32-33,36, 42-44,46-47	X	FR, A, 1126432 (DIVERSEY CORP.) 22 November 1956 see the whole document <div style="text-align: center;">--</div>	1-2,5,7,10- 11,17-18,21, 25-27,31	X	US, A, 2815311 (J.G. ELLIS et al.) 3 December 1957 see the whole document (cited in the application) <div style="text-align: center;">--</div>	1-7,11,17- 18,21,42- 44	X	US, A, 4698165 (T.W. THEYSON) 6 October 1987 see the whole document <div style="text-align: center;">--</div>	1,21-22	./.		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³																		
X	US, A, 4759852 (M.G. TRULEAR) 26 July 1988 see the whole document <div style="text-align: center;">--</div>	1-2,5-7,11- 13,16,21-22, 27,32-33,36, 42-44,46-47																		
X	FR, A, 1126432 (DIVERSEY CORP.) 22 November 1956 see the whole document <div style="text-align: center;">--</div>	1-2,5,7,10- 11,17-18,21, 25-27,31																		
X	US, A, 2815311 (J.G. ELLIS et al.) 3 December 1957 see the whole document (cited in the application) <div style="text-align: center;">--</div>	1-7,11,17- 18,21,42- 44																		
X	US, A, 4698165 (T.W. THEYSON) 6 October 1987 see the whole document <div style="text-align: center;">--</div>	1,21-22																		
./.																				
¹⁰ Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "G" document member of the same patent family																		
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; font-size: small;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black; font-size: small;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="text-align: center; padding: 5px;">27th September 1990</td> <td style="text-align: center; padding: 5px;">19. 10. 90</td> </tr> <tr> <td style="border-bottom: 1px solid black; font-size: small;">International Searching Authority</td> <td style="border-bottom: 1px solid black; font-size: small;">Signature of Authorized Officer</td> </tr> <tr> <td style="text-align: center; padding: 5px;">EUROPEAN PATENT OFFICE</td> <td style="text-align: center; padding: 5px;">Mme N. KUIPER </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	27th September 1990	19. 10. 90	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	Mme N. KUIPER										
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report																			
27th September 1990	19. 10. 90																			
International Searching Authority	Signature of Authorized Officer																			
EUROPEAN PATENT OFFICE	Mme N. KUIPER																			

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	US, A, 3147219 (L.O. PATERSON) 1 September 1964 see example 2; claims --	1-11
P,X	US, A, 4846979 (J. HAMILTON) 11 July 1989 see the whole document --	1-2, 42-47
X	DE, A, 2042254 (FISONS) 4 March 1971 see pages 1, 6-7, 10, 15-16 --	1, 21, 31, 37-42
X	US, A, 4451376 (J.D. SHARP) 29 May 1984 see the whole document (cited in the application) --	1-2, 44
P,X	US, A, 3412021 (L.O. PATERSON) 19 November 1968 see the whole document	1-11
A	(cited in the application) --	12-20
X	GB, A, 1327531 (MINES DE POTASSE etc.) 22 August 1973 see claims (cited in the application) -----	47

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9003139

SA 37891

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 15/10/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4759852	26-07-88	AU-A- 2343088	20-04-89
		EP-A- 0311954	19-04-89
		JP-A- 1130795	23-05-89
FR-A- 1126432		None	
US-A- 2815311		None	
US-A- 4698165	06-10-87	None	
US-A- 3147219		None	
US-A- 4846979	11-07-89	None	
DE-A- 2042254	04-03-71	FR-A- 2062165	25-06-71
		GB-A- 1327763	22-08-73
		NL-A- 7012770	02-03-71
US-A- 4451376	29-05-84	None	
US-A- 3412021		None	
GB-A- 1327531	22-08-73	FR-A- 2105450	28-04-72
		AT-A, B 310683	15-08-73
		BE-A- 772292	07-03-72
		CH-A- 540199	28-09-73
		DE-A, C 2143396	16-03-72
		NL-A- 7112158	10-03-72